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EVALUATION OF TECHNIQUES FOR MEASURING BIOGENIC AIRBORNE SULFUR COMPOUNDS
Cedar Island Field Study 1977

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ABSTRACT

Sulfur in both gaseous and particulate form has been measured near biogenic sources using new measurement techniques. The preconcentration of gaseous sulfur on gold-coated glass beads followed by desorption into a flame photometric detection for sulfur is shown to have a detection limit of 0.1-0.2 ng of sulfur and to allow for speciation of H_2S, CH_3SH and $(CH_3)_2S$ at low parts per trillion levels. Ambient levels of NO_2 and O_3 were found to alter the molecular form of sulfur on the beads unless scrubbed from the sampled air. A collection technique using tandem filters is extended from earlier efforts on fine and coarse aerosol to include collection of SO_2 and H_2S on chemically coated filters; these filters are analyzed by X-ray fluorescence for sulfur content. Measurements of gases evolved from biogenic sources reveal H_2S and $(CH_3)_2S$ as primary components with significant diurnal variations. Recommendations for further instrument development are given.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AIB	-- Atmospheric Instrumentation Branch
atm	-- atmosphere
cc	-- cubic centimeter
CIFS	-- Cedar Island Field Study
cm	-- centimeter
CSI	-- Columbia Scientific Instruments
DST	-- daylight savings time
EPA	-- Environmental Protection Agency
ERC	-- Environmental Research Center
FPD	-- flame photometric detector
ft	-- feet
g	-- gram
GPT	-- gas phase titration
H	-- high tide
hr	-- hour
ID	-- inside diameter
in	-- inch

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS (Continued)

kW	-- kilowatt
L	-- low tide
l	-- liter
m^2	-- square meter
m^3	-- cubic meter
max	-- maximum
MDL	-- minimum detectable level
min	-- minute
ml	-- milliliter
MT	-- megaton
MV	-- maximum measured value
ng	-- nanogram
nm	-- nanometer
NSF-RANN	-- National Science Foundation -- Research Applied to National Needs
OD	-- outside diameter
ppb	-- parts-per-billion
ppm	-- parts-per-million
psig	-- pounds-per-square-inch-of-gravity
RH	-- relative humidity

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS (Continued)

RS	-- unseparated sulfur compounds in the sample released from cold trap into the Meloy
RTP	-- Research Triangle Park
sec	-- second
T	-- temperature
TFP	-- tandem filter pack
TS	-- total sulfur
TSP	-- total sulfur particulate
UV	-- ultraviolet
v/v	-- volume-per-volume
WD	-- wind direction
WS	-- wind speed
yr	-- year

SYMBOLS

$AuCl_3$	-- gold chloride
CCl_2F_2	-- Freon 12
CCl_3F	-- Freon 11
$CH_3CHOHCH_3$	-- isopropanol
CH_3CSNH_2	-- tioacetamide

LIST OF ABBREVIATIONS AND SYMBOLS

SYMBOLS (Continued)

$(CH_3)_2S_2$	-- dimethyl disulfide
$(CH_3)_2S$	-- dimethyl sulfide
COS	-- carbonyl sulfide
CO	-- carbon monoxide
C_2H_4	-- ethylene
C_2H_5SH	-- ethyl mercaptan
$Cu(NO_3)_2$	-- copper nitrate
HCl	-- hydrochloric acid
H_2S	-- hydrogen sulfide
H_2SO_4	-- sulfuric acid
H_3O_4P	-- phosphoric acid
μm	-- micron
$NaCO_3$	-- sodium carbonate
NaOH	-- sodium hydroxide
$N(CH_2CH_2OH)_3$	- triethanolamine
NH_3	-- ammonia
NH_4Cl	-- ammonium chloride
NO	-- nitric oxide
NO_2	-- nitrogen dioxide
NO_x	-- nitrogen oxides
N_2O	-- nitrous oxide

LIST OF ABBREVIATIONS AND SYMBOLS

SYMBOLS (Continued)

O_3	-- ozone
S	-- sulfur
SO_2	-- sulfur dioxide

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SECTION I

INTRODUCTION

The Cedar Island Field Study (CIFS), conducted from August 22, 1977 to September 2, 1977, was a concentrated effort to monitor selected gaseous and particulate species at an isolated location on the North Carolina coast. Prototype instrumentation and newly developed measurement techniques were used. The gold-coated glass bead technique (1) for the sampling and preconcentration of volatile sulfur compounds was of particular interest: the CIFS provided the first chance to evaluate this technique in a field test. The use of a tandem filter technique (2) was also of considerable interest as it has recently been adapted (3) to measure hydrogen sulfide (H_2S) and sulfur dioxide ($SO_{2)}$ as well as coarse and fine particulate.

The objective of the CIFS was to establish the status of instrumentation development with respect to the volatile sulfur compounds which are of biogenic origin as well as those gases which influence the composition of biogenic emissions at receptor locations, e.g., ozone (O_3). Information pertaining to the elemental composition of particulate matter, meteorological parameters, and the species of sulfur compounds emitted

from nearby marsh areas were recorded so that variations in the ambient mix of the sulfur compounds could be related to characteristics of the particular air mass being sampled.

Many of the activities related to the CIFS represent learning experiences for the AIB staff. These experiences will lead to a better appreciation of the effort needed to launch a field study and to sustain a concentrated monitoring effort in the field. Furthermore (and most importantly), the performance characteristics of various instruments under field conditions have focussed attention on instrumentation needs, resulting in a set of recommendations for future initiatives. These initiatives should help to better define the relationship between biogenic emissions of sulfur, nitrogen, and carbon compounds, and the atmospheric loading of sulfate, nitrate, and carbonate particulate.

SECTION 2

EXPERIMENTAL PROCEDURES

THE CEDAR ISLAND FACILITY

The Cedar Island National Wildlife Refuge on the coast of North Carolina was selected as the site for the summer 1977 field test. As shown in Figure 1, the Refuge is adjacent both to extensive marsh lands and to the sheltered waters between the Outer Banks and the North Carolina mainland. Initial survey trips to the island confirmed that the area was isolated from traffic and that adequate support facilities were available.

The stationary monitoring site on Cedar Island is shown in Figure 2. Two areas were prepared for the field test. One of these was a room in the blockhouse shown in Figure 2. The room was cleared and an air conditioner was installed in anticipation of the intensive staff effort to come. An area adjacent to the blockhouse was prepared for a mobile van which was to house several air monitoring instruments. The van was supplied with electrical power of up to 12 kW from the blockhouse.

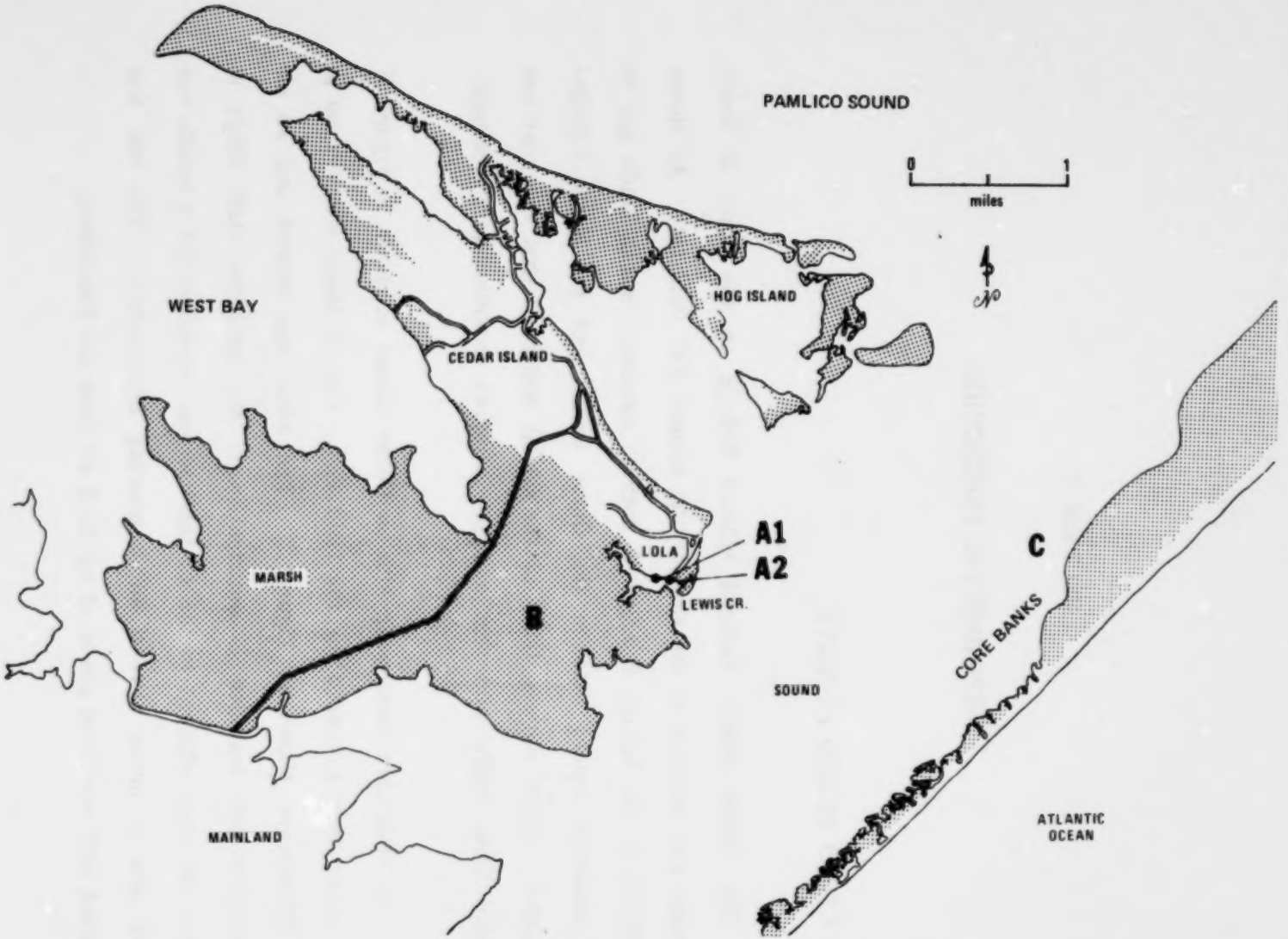

Figure 1. Cedar Island and surroundings - Lola is at 76° 17′ 13″ longitude and 34° 57′ 30″ latitude.

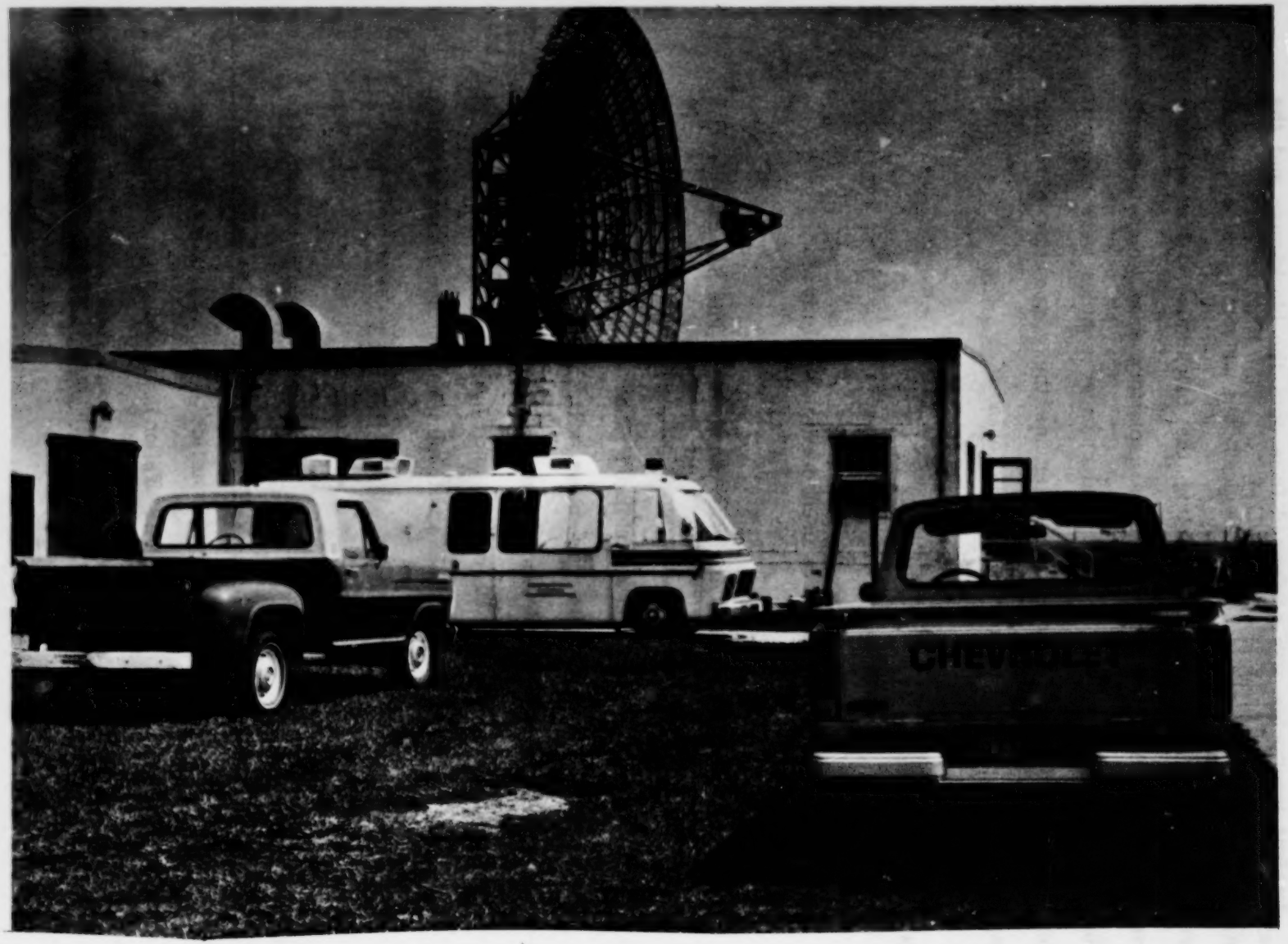

Figure 2. Blockhouse, Mobile Van, Radar Antenna and Sound at the Cedar Island Wildlife Game Refuge

Ambient monitoring was performed from both the blockhouse and the van. Particulate and gas collection devices and meteorological equipment were deployed in the yard surrounding the blockhouse. The antenna structure shown in Figure 2 was used as a platform from which to sample ambient sulfur compounds. Environmental chamber samples were taken at Sites A, B, and C of Figure 1 to determine the composition of sulfur compounds being emitted from the local land areas.

INSTRUMENTATION

The following instruments were used during the study:

1. Meloy SA 285 Total Sulfur Analyzer SN 6DO63: The SA 285 provides for thermal control of the burner block, photomultiplier, and flow control devices to achieve a stabilized flame and a detection limit of 0.5 ppb, i.e., twice the rms noise with a time constant of 0.7 seconds. Sample air is drawn continuously through the detector at a controlled flow rate of 200 cc/min and hydrogen for the flame is supplied at 190 cc/min. Some additional performance characteristics are given in Appendix B.

2. Tracor 560 Gas Chromatograph with Flame Photometric Detector: The Tracor 560 resolves H_2S, SO_2, methyl mercaptan (CH_3SH), ethyl mercaptan (C_2H_5SH), and dimethyl sulfide ($(CH_3)_2S$) using a column (36 in long, 1/8 in OD of FEP Teflon) packed with 60/80 mesh Chromosorb T coated with polyphenyl ether and conditioned

with phosphoric acid (H_3O_4P). Using a column temperature of 60°C and a flow rate of 100 cc/min of nitrogen carrier, a 10 ml sample provides a sensitivity of 3 ppb for H_2S, SO_2, and CH_3SH, and of 7 ppb for the remaining compounds, based on peak height.

3. Meloy SA 185 Total Sulfur Monitor: The SA 185 is a commercial flame photometric detector (FPD) used to monitor sulfur compounds. It is less sensitive than SA 285 and is used with a preconcentration technique to detect ambient sulfur. The detection limit is 2 ppb with a 5 sec time constant.

4. Columbia Scientific Instruments (CSI) Series 1600 Oxides of Nitrogen Analyzer: The CSI Nitrogen Analyzer is new to the commercial market. Several features such as temperature control of critical orifices in the sample and O_3 inlet lines and of the reaction chamber appear to enhance instrument performance at low ppb levels. A detection limit of 0.5 ppb is achieved with a 60 sec time constant.

5. AeroChem Chemiluminescence Nitrogen Oxides and Ammonia Monitor: This research prototype incorporates a high temperature platinum converter for ammonia (NH_3) to nitric oxide (NO) conversion, a high sample flow rate and a spiral reaction chamber to keep the NO - O_3 reaction close to the system's photomultiplier. The instrument is built for aircraft use. The detection limit is 0.5 ppb with a 24 sec time constant.

6. Bendix Ozone Analyzer, Model 8002: This commercial O_3 analyzer is based on the chemiluminesence of O_3 and excess ethylene (C_2H_4). The detection limit is 2 ppb with a 3 sec time constant.

7. Dasabi Ozone Analyzer, Model 1003-AH: This commercial O_3 analyzer is based on the absorption of mercury resonance radiation at 2537 Å. The detection limit is 2 ppb with a 1 min digital update.

8. Climet Portable Meteorological Station, Model EWS: This instrument measures wind speed, wind direction, temperature, and relative humidity.

9. Manual Dichotomous Sampler: This sampler is used for particulate collection and size fractionation in two ranges with the cut point between fine and coarse particle fractions at 3.5 μm particle diameter and the upper cutoff at about 20 μm.

10. Tandem Filter Sets: This sequence of four filters collects fine particulate, coarse particulate, H_2S, and SO_2. See detailed explanation in text.

11. Collection Tubes and Accessory Equipment for the Gold-Coated Glass Bead Preconcentration Technique: This method is being developed by Dr. R. Braman and Mr. M. Ammons of the University of South Florida under the sponsorship of the National Science

Foundation -- Research Applied to National Needs (NSF-RANN) -- to measure ambient sulfur compounds with existing FPD instrumentation. See detailed explanation in text.

12. Portable Calibration System: This system provides a double dilution stage which gives low ppb levels using standard permeation tubes. The system uses mass flow controllers to regulate air flow over a temperature controlled permeation tube (first dilution) and through a dilution stream (second dilution). A glass capillary allows a fraction of air from the first dilution stream to mix with the second dilution stream. This unit is one-of-a-kind made by the Research Triangle Institute, Research Triangle Park (RTP), North Carolina, for the Environmental Protection Agency (EPA).

13. Gas Phase Titration Apparatus for Nitrogen Oxides and Ozone Calibration: The unit assembled for this field trip used electronic flow controllers and gas mixing chambers. As suggested by Rehme, et al. (4), it was used with a secondary standard NO cylinder.

14. Portable Bag Samplers and Constant Flow Pump System: These were used for sample collection on the gold-coated glass bead traps.

These instruments were used according to the schedule given in Table 1.

TABLE 1. INSTRUMENT UTILIZATION

Instrument	Parameter Measured	AUGUST M 22	T 23	W 24	T 25	F 26	S 27	S 28	M 29	T 30	W 31	SEPTEMBER T 1	F 2	S 3	S 4
AeroChem	$NO_x + NH_3 + \ldots$		—												
Bendix 8002	O_3	———	—	———		———		— —	———						
Climet	WSWD, RH, T		———												
CSI	NO		—												
	NO_2	— ———		———	—										
	NOx					———	—								
Dasibi	O_3	———	--					———							
Dichotomous Sampler	Fine Particulate		———												
	Coarse Particulate		———												
Gold Beads Preconcentrator	H_2S	———													
	$(CH_3)_2S$	———													
Meloy 285	TS	———													
	$TS-SO_2$	———													
Tandem Filters	Fine		———												
	Coarse		———												
	H_2S		———												
	SO_2		———												
Tracor	H_2S, $(CH_3)_2S$, etc		———												

MEASUREMENT OF AMBIENT SULFUR

Both gaseous and particulate sulfur were measured during the CIFS. Gaseous sulfur compounds were marginally detectable by direct, real-time measurement techniques. Preconcentration techniques were used for a more definative measurement. Particulate sulfur samples were collected on filters over 24 hour sampling periods.

Gaseous Sulfur Compounds by Flame Photometry

The FPD is used routinely in ambient monitoring of sulfur gases. The FPD is based on the reactions attendant to burning gaseous sulfur compounds in a hydrogen-rich flame (5). One reaction leads to the formation of excited sulfur which can de-excite with the emission of a photon (300-450 nm). Separation of sulfur compounds on a gas chromatographic column prior to analysis in the flame allows for speciation. In commercial instrumentation an interference filter centered for maximum transmission at 394 nm is positioned between the flame and a photomultiplier and defines the instrument's response characteristics.

For the CIFS, the Meloy Model SA 285 was chosen as a total sulfur monitor (see Instrumentation). Hydrogen sulfide and SO_2 were detected separately by using chemical in-line scrubbers supplied by Meloy.

The Model 560 Tracor Chromatograph with an FPD was chosen for the study. A gas chromatographic column similar to that described by Stevens, et al. (6), separated the sulfur compounds. The column is described under Instrumentation. The retention times for the column were as follows: H_2S and carbonyl sulfide (COS), 1.3 min.; CH_3SH, 4.1 min; $(CH_3)_2S$, 6.4 min.

Calibration was performed using permeation tubes of the individual gases to be measured. The tubes were weighed on a Cahn electrobalance to determine permeation rates at set temperatures. Both preliminary and field calibrations were performed with a prototype portable calibration system capable of generating less than 1 ppb of the sulfur gases at flow rates required by the FPD instrumentation.

The zero air (carbon dioxide (CO_2) in air) used in calibration was obtained from Scott-Marrian, Inc. and contained less than 1 ppb of SO_2. Both the zero air and calibration mixtures were humidified to a relative humidity of 60-90%. Initial calibration was performed at the Environmental Research Center (ERC) Annex prior to the CIFS and consisted of a multipoint calibration of the Meloy SA 285 using H_2S and a multipoint calibration of the Tracor 560 for H_2S using peak height and for $(CH_3)_2S$ using peak area. Hydrogen sulfide response on the Meloy SA 285 was linear with a nearly constant sensitivity of 1.11 $\pm$ .01 ppb/chart division for H_2S and of 0.91 $\pm$ .01 ppb/chart division for $(CH_3)_2S$. These sensitivity checks were consistent during daily span checks at Cedar Island from

August 23 until September 1, and again following a 2-day study September 23 and 24. The Tracor 560 was initially calibrated in the laboratory and checked in the field for H_2S and $(CH_3)_2S$. Gas chromotographic column performance deteriorated during the study with a significant reduction in sensitivity. The total sulfur minus the SO_2 readings on the Meloy were no more than 20% higher than the H_2S plus $(CH_3)_2S$ readings on the Tracor 560 during analysis of the emission products from Cedar Island marsh areas, indicating the presence of some low concentrations of higher molecular weight sulfur compounds.

Gaseous Sulfur Compounds by Preconcentration of Gold-Coated Glass Beads

The concentration of H_2S and organosulfur compounds in ambient air is often too low for direct detection by an FPD. However, the sulfur compounds in a large volume of ambient air can be collected; they can then be released from the collection surfaces in considerably less time than it took to collect them. This method can be used to raise the sulfur compound concentrations above the lower detection limit of the FPD. The original ambient air concentrations can then be estimated if the efficiency of collection and of release are known and prior calibration is available.

Ammons (7) studied a variety of metal surfaces for collection of sulfur-containing molecules and selected gold. Method development related to the use of gold-coated glass beads as a collection medium has

been carried out at the University of South Florida under the direction of Dr. R.S. Braman with the sponsorship of the NSF-RANN. Technical information exchange between the groups at the University of South Florida and EPA led to the use of collection techniques in the CIFS. The CIFS was the first environmental study to test of the gold-coated glass bead technique.

The sample collection of sulfur compounds using the gold coated glass bead technique occurs when a measured volume of ambient air is pulled through 1 cm ID quartz tubes packed with a 3 cm length of 60/80 mesh gold coated glass beads held in place with quartz wool. Measurements with the technique consist of five steps: 1) blanking of the collection tubes; 2) collection of an ambient sample; 3) desorption of collected molecules from the beads onto a liquid nitrogen-cooled, cold trap; 4) release from the cold trap into a FPD; and 5) reblanking of the collection tube.

Blanking establishes the signal response from a "clean" collection tube. Blanks taken before and after the collection and analysis of sample air are averaged to obtain the zero response. The zero response varies depending on the batch of glass beads being used and their previous use. A typical blank for H_2S during the CIFS was 1-2 ng/sample with an uncertainty estimated at 0.1-0.2 ng/sample. Typical sample responses for H_2S were 5-10 ng/sample. No blank response for $(CH_3)_2S$ and CH_3SH was evident.

Ambient air samples were taken by attaching a small electric air pump to the tube through a line containing a critical orifice. Samples of up to 30 minutes were taken at a flow rate of 2 l/min. After collection, the collection tube was connected to a nitrogen-cooled, cold trap as shown in Figure 3. The U-shaped cold trap was packed for over half its length with 60/80 mesh glass beads. Hydrogen gas was passed through the tube at a flow rate of 100 cc/min and the tube was heated to 600°C by a coil of 20 gauge nichrome wire. At the end of a 5-minute period the desorption of sulfur compounds from the tube onto the cold trap was complete. The liquid nitrogen was then removed from the trap and nitrogen gas was passed through the trap for approximately 20 seconds as shown in Figure 4. The trap was then heated and the trapped sulfur compounds desorbed in order of boiling points. The nitrogen was vented to a "T" connection at the intake to a Meloy SA 185. The total flow into the Meloy SA 185 consisted of the nitrogen and sulfur-free air supplied at the "T". A recorder, Linear Instruments, Model 252 A, was used with the Meloy. A typical output recorder trace for H_2S, CH_3SH and $(CH_3)_2S$ is shown in Figure 5. The recorder also provided for integration of area under the individual peaks.

Typical ambient concentrations encountered at Cedar Island were: H_2S = 80 ppt; $(CH_3)_2S$ = 30 ppt; and dimethyl disulfide ($(CH_3)_2S_2$) = 20 ppt. Samples collected for 30 minutes at 2 l/min resulted in a sulfur loading of 8 ng H_2S, 3 ng $(CH_3)_2S$, and 4 ng $(CH_3)_2S_2$, as compared to an uncertainty in the collection tube blank of 0.1-0.2 ng.

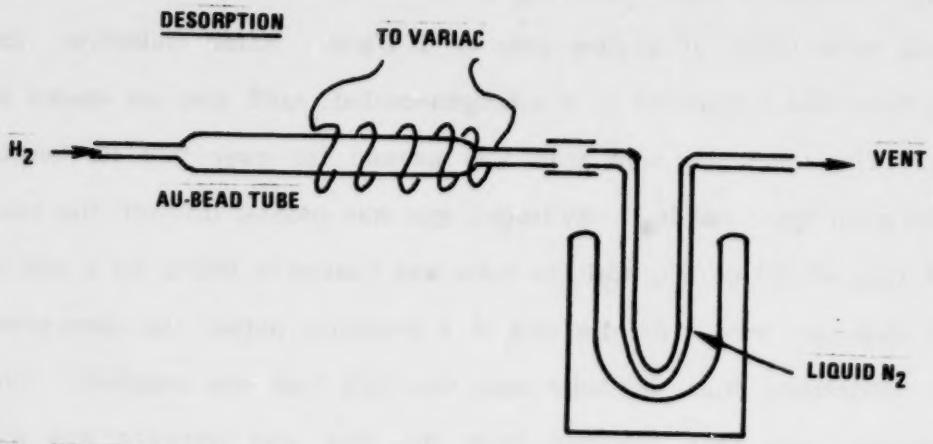

Figure 3. Apparatus for desorption of preconcentrated sulfur compounds to cold trap.

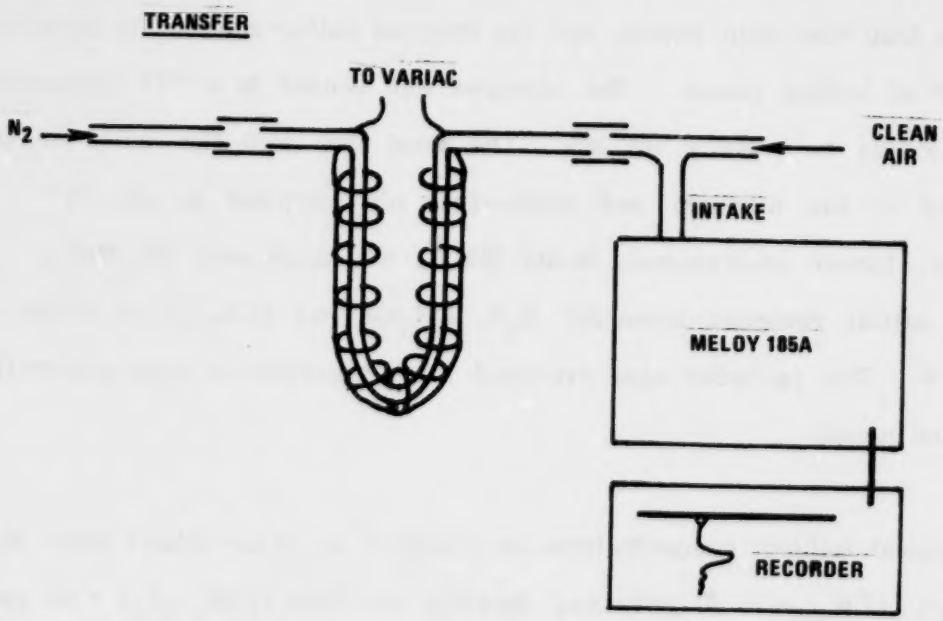

Figure 4. Apparatus for transfer of sulfur compounds from cold trap.

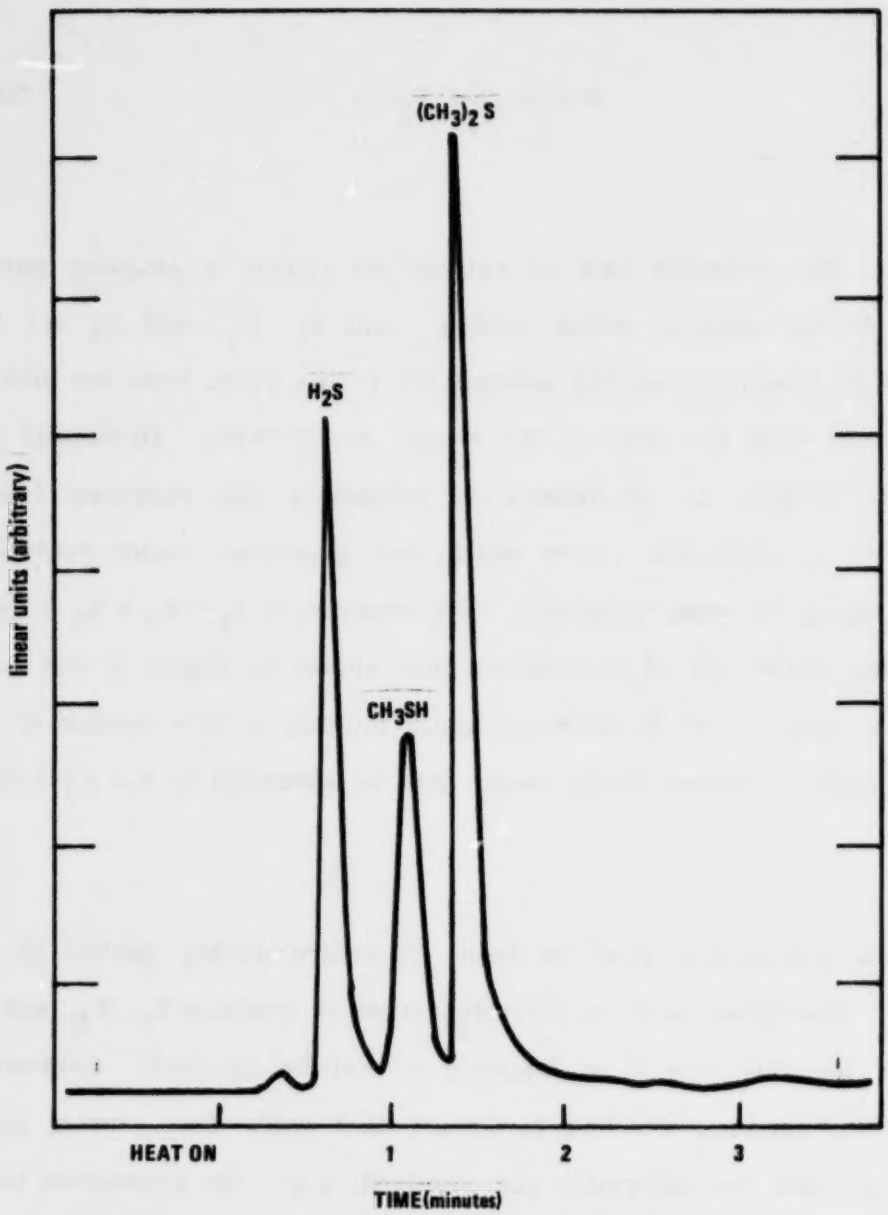

Figure 5. Recorder trace of sulfur compounds desorbed from liquid nitrogen-cooled, cold trap after preconcentration step.

Stated mathematically, the response "R" of the Meloy, assuming that the photomultiplier signal is linearized with respect to sulfur gas concentration, is such that:

$$R \sim FL_A E_1 E_2 E_3 \Delta T, \qquad \text{(Eq. 1)}$$

where F is the collection rate of ambient air during a sampling period "ΔT", L_A is the ambient sulfur loading, and E_1, E_2, and E_3 are the efficiencies of transfer from the ambient air to the tube, from the tube to the trap, and from the trap to the Meloy, respectively. Ordinarily the ambient air loading is determined by comparing the response (chart divisions) to a calibration curve which was generated under controlled conditions using the same apparatus. For example, if $E_1 = E_2 = E_3 = 1$ and a calibration curve for H_2S such as that shown in Figure 6 has been obtained, a response of 20 divisions would indicate a tube loading of 6.5 ng. The ambient concentrations could then be estimated as 6.5 ng/FΔT in ng/l.

Several precautions must be taken to insure quality control of the technique. Quantities such as the efficiencies of transfer E_1, E_2, and E_3 as well as the flow rate F in Equation 1 must be checked. Calibration concentrations must be checked to ensure that sulfur-free carrier gases are used and that the calibration gas standard, e.g., the permeation tube, is accurately characterized.

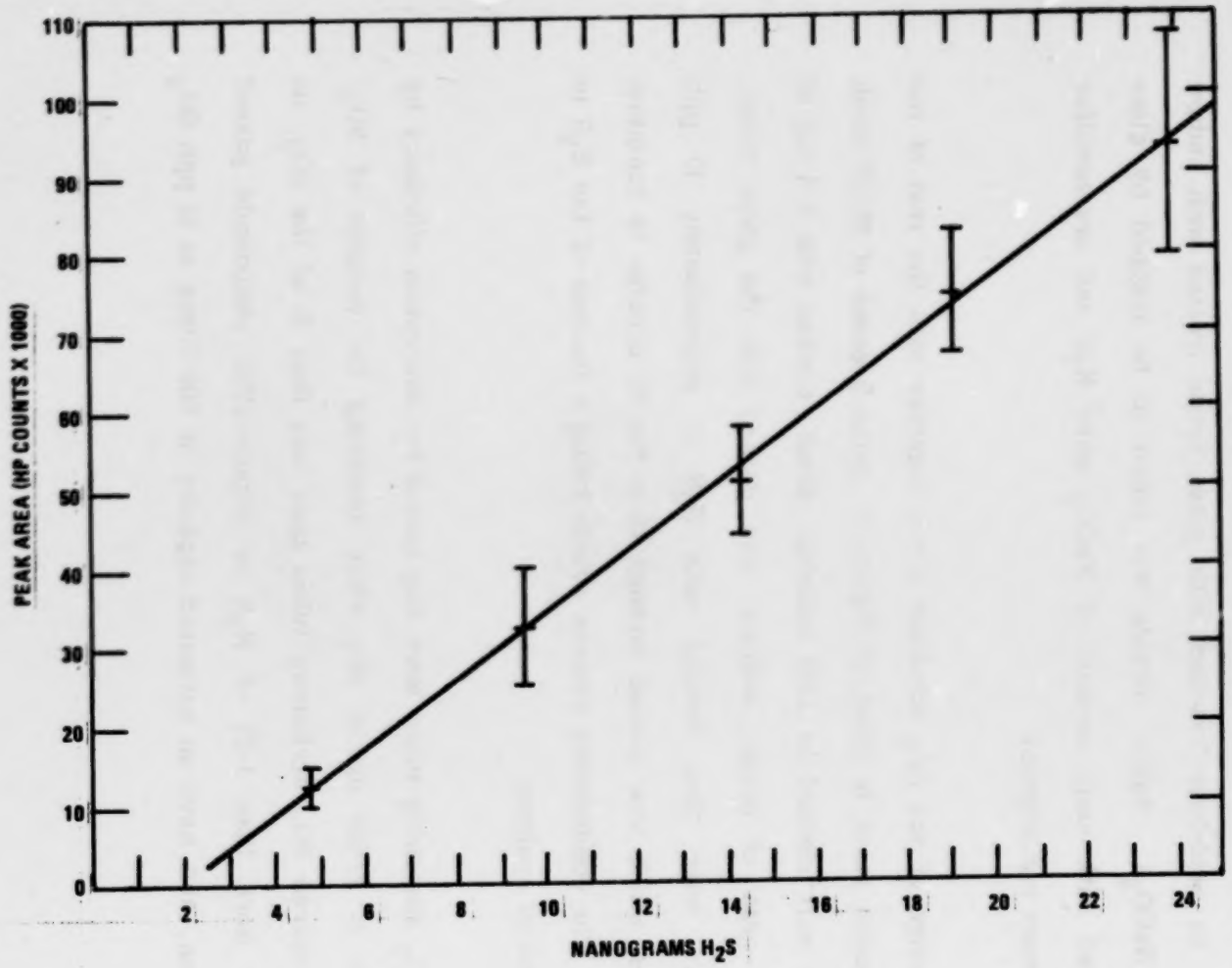

Figure 6. Calibration curve for H_2S by Bennett (EPA). HP refers to a Hewlett Packard Integrator.

Sulfur Dioxide Scrubbers

Sulfur dioxide has the most potential to interfere in the detection of reduced forms of sulfur and must be removed prior to trapping. This is done using an acid-base reaction with glass beads treated with sodium carbonate ($NaCO_3$). Sulfur dioxide was found to be trapped by glass beads treated with small amounts of $NaCO_3$ while H_2S and organosulfur compounds were not trapped.

The design of the SO_2 scrubber tubes together with the rest of the preconcentration stack is shown in Figure 7. Some 5 grams of 80/120 mesh glass beads were cleaned by acid washing, dried, treated with 8.4 mg of $NaCO_3$ per gram of beads, redried, and packed into the glass tubes. These tubes were then treated with H_2S at approximately 10 ppb concentration which was passed through them for 30 minutes to condition the tubes. The conditioning process avoids losing a fraction of the H_2S in the first several analyses.

The SO_2 absorbing tubes were also tested for absorption efficiency by the addition of 10-100 ng of SO_2 while analyzing for passage of SO_2. Suitably prepared SO_2 scrubbing tubes pass less than 1% of the SO_2, do not absorb more than 1-2% of H_2S or organosulfur compounds passed through them, and have an estimated capacity of 500 liters at 10 ppb SO_2 levels.

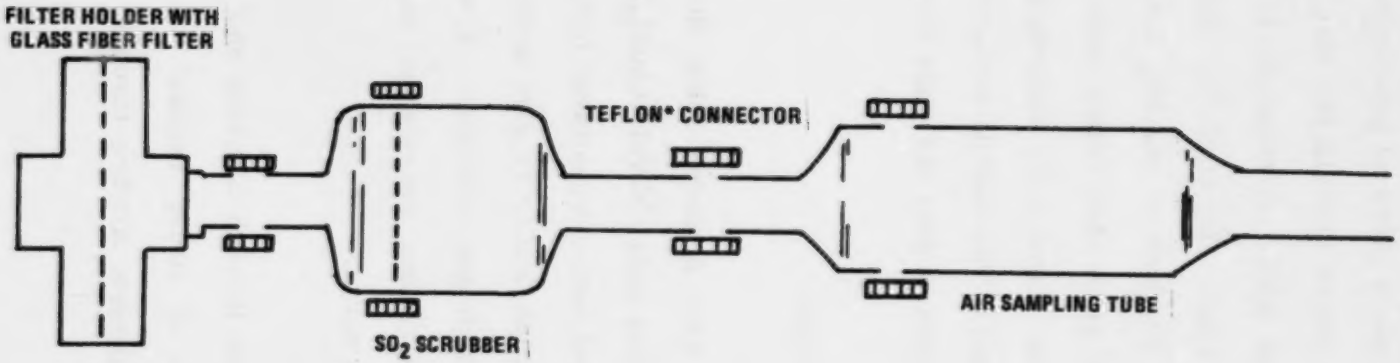

Figure 7. Typical SO_2 scrubber tube.

Particulate Filters

Sulfate particulates are also a potential interferent if they are allowed to collect on the beads. As shown later in the text, the average loading of particulate sulfur at Cedar Island corresponds to approximately 14 ng for a 30-minute sample at 2 l/min. To avoid this type of interference, a particulate filter was placed in front of the SO_2 scrubber-collection tube combination. Gelman Type A glass fiber filters were used throughout the tests except for Tower studies 4 and 5 (as described later) in which 0.2 μm Nuclepore filters were used. The volatile sulfur compounds SO_2, H_2S, CH_3SH, and $(CH_3)_2S$ were found to pass the glass fiber filters.

Preconcentration Tube Preparation

Preconcentration tubes were prepared using 60/80 mesh glass beads (Varian Instruments, Inc.) and gold chloride ($AuCl_3$) prepared from gold foil. The beads were washed with concentrated hydrochloric acid (HCl), dried, and treated with enough $AuCl_3$ to give approximately a 10% (wt.) coating of gold metal after hydrogen reduction. The sampling tubes were approximately 8 in long, including connectors, and were packed with approximately 3 cm of coated beads.

Prepared tubes were put through blanking and efficiency tests prior to use. Blanking consists of simply heating the tube while passing hydrogen or a hydrogen-nitrogen mixture through for 5 minutes. Any

residual sulfur is transferred to the cold trap and to the Meloy, as in a standard analysis. If blanks are not easily reduced to a low value, the tube is washed with a few milliliters of concentrated HCl, washed with water, and then reblanked. Blank values of 1-2 ng and sometimes lower should be attainable although sulfate sulfur is often only slowly removed from the tubes.

Gold-coated tubes may be used repeatedly. No specific test has been conducted to confirm this, but some gold tubes have been used over fifty times in laboratory experiments. Acid washing reduces the useful tube life by loosening the gold coating on the beads.

Small pieces of organic matter on the tubes turn to carbon during analysis and can absorb sulfur compounds if used again. Tubes can be cleaned of carbon contamination by heating the tubes to analysis temperature in the presence of oxygen. Organic compounds in air samples apparently do not cause this type of interference.

In later work the glass beads were found to contain small amounts of sulfur compounds which slowly reduce and produce the small blanks encountered. The beads were also found to contain substantial amounts of iron and zinc; compounds of these elements are generally removed in the bead cleaning process with acid or by oxidation with oxygen while heating the tubes to 700-800°C. Iron is a particularly troublesome interferent and should be removed from all parts of the analysis system which encounters the sample.

Standards and Calibration

Two types of standards have been studied for calibration of the FPD detectors used in sulfur air analyses and for determining the operational characteristics of the analysis system. These are the permeation tube standards of the type developed by O'Keeffe and Ortman (8), as well as the aqueous solutions of thioacetamide (CH_3CSNH_2).

Thioacetamide in aqueous solutions was found to be a good reproducible calibration standard for H_2S. Stock solutions (approximately 2000 ppm) were diluted to 4 ppm and microliter sized samples of the latter were injected onto gold-coated bead columns. The reproducibility of thioacetamide standards was found to be $\pm$ 4.9% relative for 21 samples of 16 ng H_2S on five different gold tubes. A comparison of two gold tubes indicated no significant difference at the 80% confidence interval. Similar reproducibility was experienced using permeation tubes as standards for H_2S, $(CH_3)_2S$, CH_3SH, and SO_2.

Ammonium chloride (NH_4Cl) and sulfuric acid (H_2SO_4) were also tested as standards. The thioacetamide was the most stable calibration standard over a period of time. This standard was compared to weighed permeation tube standards using the Meloy SA 185 detector in work at Cedar Island. Figure 8 shows that both give approximately the same calibration curve.

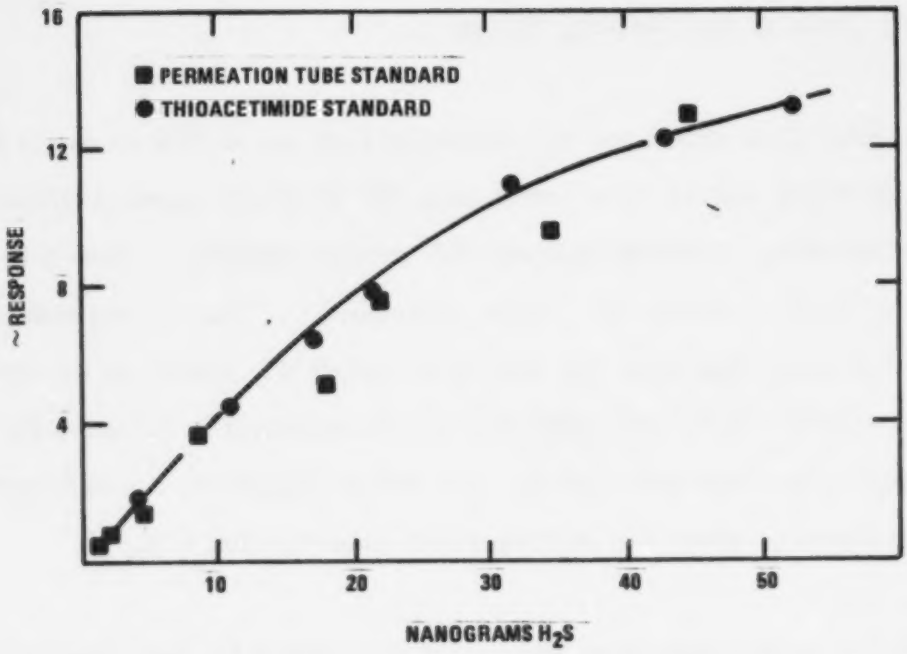

Figure 8. Comparison of permeation tube and thioacetimide standards.

Figure 9 shows the calibration curve data obtained for H_2S, $(CH_3)_2S$, and CH_3SH using U-trapped standards and the Meloy 185 FPD. Despite the linearizer on the detector instrumentation, some curvilinear character is observed in these calibration curves. This is not surprising since fluorescence self absorption effects are involved and must be a function of sample size.

Efficiency Tests of the Sampling System

All gold tubes tested for H_2S retention from air at flow rates up to at least 3 liters per minute show better than 99% efficiency under a variety of humidity conditions between 50% and 95% relative humidity. Gold tubes do exhibit a finite capacity for sulfur compounds. This is approximately 500-1000 ng depending upon the gold tube tested but related to the amount of gold present. Since the gold tube preconcentration is intended for use with sample sizes well below 100 ng, the sulfur capacity is not approached. A similar capacity effect and efficiency was observed for $(CH_3)_2S$.

Several comparisons were made of H_2S adsorbed by and removed from the gold tubes versus the H_2S evolved from the permeation tube dilution system; no difference was noted. The agreement of the thioacetamide standards to the diffusion tube standards also supports the H_2S efficiency observed. No losses of H_2S, $(CH_3)H_2S$, or CH_3SH were noted on either the glass fiber filters or in the SO_2 scrubbing tubes.

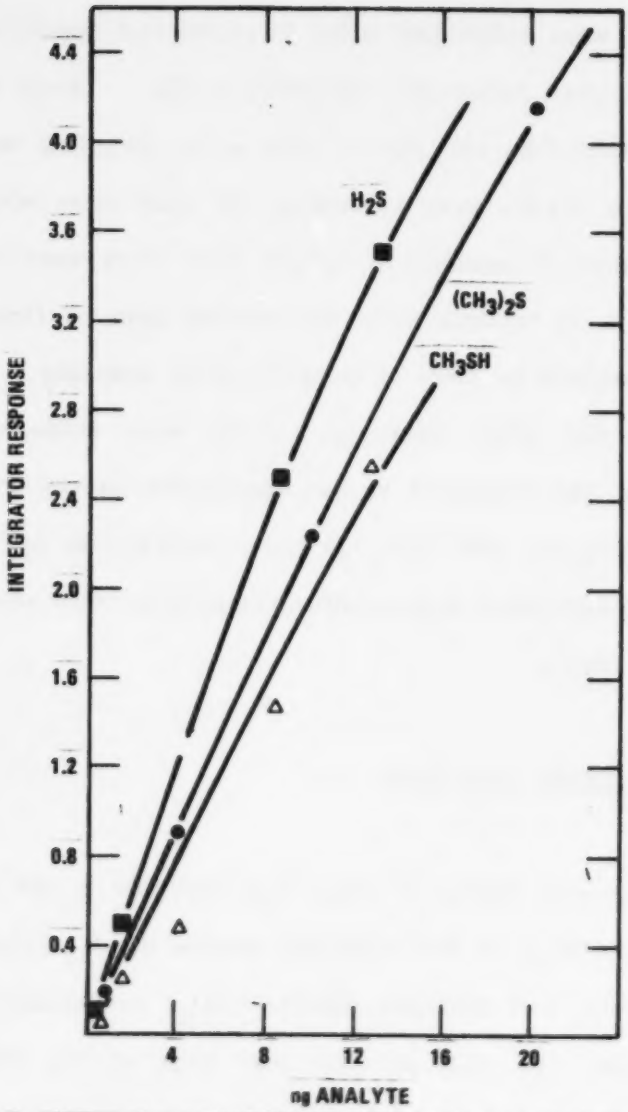

Figure 9. Calibration data for H_2S, $(CH_3)_2S$, and CH_3SH.

Procedure for Sampling and Analysis

Several routine procedures for sampling and analysis were adopted. Gold sampling tubes were reblanked prior to reuse and assembled with the filters and SO_2 scrubber tubes into sampling stacks. These were sealed with laboratory paraffin film and stored until used. Sampling was timed by stopwatch. Sampling stacks were calibrated for flow rates while attached to the same pump used in sampling. Sample flow rates were found to be reproducible within ± 5% relative over the several days of field sampling. Gold tubes were analyzed as soon as possible after sampling. Tubes were also reblanked directly after sampling. Data were obtained using an integrating recorder and compared to the calibration curves for analyses. Hydrogen sulfide, CH_3SH, and $(CH_3)_2S$ were reported in ng/liter and in ppb by volume. Unidentified organosulfur compounds were analyzed using the H_2S calibration curve.

Effects of Nitrogen Oxides and Ozone

A sometimes ignored aspect of trace H_2S analysis is the effect of O_3 and nitrogen oxides (NO_x) on the collection system used. From the known oxidizing nature of O_3 and nitrogen dioxide (NO_2) one would predict that either should oxidize H_2S and perhaps also some of the other reduced forms of sulfur. Moreover, the amounts of O_3 and nitrogen present in air are generally much larger than the H_2S or other reduced forms of sulfur present. Non-urban concentrations of NO_2 and O_3 are in the 5-20 and

5-50 ppb concentration range according to recent reviews (9). Since H_2S may be expected to be from 0.05-1.0 ppb, it is apparent that the oxidizers form a substantial excess.

Preliminary experiments indicated that NO_2 and O_3 oxidize sulfur compounds trapped on gold surfaces while nitrous oxide (N_2O) had no effect. Nitric oxide does not appear to be an interferent although it oxidizes to NO_2 which is an interferent.

The effect of NO_2 and O_3 on H_2S and $(CH_3)_2S$ collected on gold tubes was studied in laboratory apparatus designed to produce low concentrations of these gases. Nitrogen dioxide was supplied by a syringe-driven apparatus and diluted by air. The NO_2 concentration was analyzed by the Saltzman (10), method. Ozone was produced at low concentrations by a Welsbach Instrument Co. O_3 generator and determined by iodometric titration. Samples of H_2S and $(CH_3)_2S$ were pumped onto blanked gold tubes from a dynamic gas sampling system employing permeation tube standards. The tubes were then exposed to various amounts of O_3 or NO_2 and analyzed for sulfur compounds.

This type of experiment was carried out both with and without the use of the SO_2 scrubbing tubes to determine if the latter afforded protection against the oxidizing compounds. Tables 2 and 3 give the results of the two studies.

Unprotected tubes lose H_2S, probably as SO_2 displaced from the tubes by the oxidizing agents which were present in amounts sufficient to entirely saturate the absorption sites on the gold. Dimethyl sulfide is altered in form to H_2S. In both cases, the use of an SO_2 trap reduces the interference effects to an acceptable extent.

Similar experiments were carried out using outside air sampling at the University of South Florida. Ozone was 30-50 ppb during the time of the experiments; NO_2 was not determined at the time. The outside air may be considered an urban type air as the experiment was carried out in the city of Tampa, Florida. The results, shown in Table 4, indicate that unprotected tubes having H_2S or $(CH_3)_2S$ on them exhibit losses if air samples exceed 24 liters in volume. This is in accord with laboratory experiments which showed that the exposure of tubes to more than a few micrograms of O_3 caused losses of sulfur compounds or demethylation. Use of SO_2 absorption tubes afforded protection in the CIFS.

TABLE 2. EFFECT OF NO_2 ON H_2S RECOVERY

H_2S present	H_2S recovered	%	NO_2 Concentration	NO_2 Amount
Tubes Not Protected				
11.5 ng	11.5 ng	100%	20 ppb	120 ng
11.5 ng	6.9 ng	60%	28 ppb	430 ng
11.5 ng	5.6 ng	49%	43 ppb	1060 ng
11.5 ng	1.4 ng	12%	140 ppb	1710 ng
With SO_2 Scrubber				
11.5 ng	11.6 ng	101%	25 ppb	305 ng
11.5 ng	10.4 ng	90%	12 ppb	824 ng
11.5 ng	12.0 ng	104%	105 ppb	2600 ng
11.5 ng	5.2 ng	45%	138 ppb	3420 ng

*The amount column is the product of the concentration expressed as ng/l, the collection flow rate and the time of collection.

TABLE 3. EFFECT OF O_3 ON H_2S AND $(CH_3)_2S$ RECOVERY

Tubes Not Protected[a]			
H_2S Present	H_2S recovered	%	O_3
11.5 ng	10.5 ng	91%	6.64 µg
11.5ng	10.0 ng	87%	13.3 µg
11.5 ng	8.6 ng	75%	19.9 µg
11.5 ng	4.5 ng	39%	33 µg
$(CH_3)_2S$ Present	$(CH_3)_2S$ Recovered	H_2S found	O_3
28.6 ng	13 ng (46%)	4.9 ng	0.66 µg
28.6 ng	6.7 ng (23%)	6.4 ng	3.3 µg
28.6 ng	12.3 ng (39%)	9.2 ng	6.6 µg
28.6 ng	1.8 ng (6%)	6.0 ng	33.0 µg

[a]Two experiments with SO_2 scrubbers gave 100% recovery of $(CH_3)_2S$.

TABLE 4. EFFECT OF OUTDOOR AIR ON $(CH_3)_2S$ RECOVERY

$(CH_3)_2S$ Present	$(CH_3)_2S$ Recovered	%	Air Volume	Air Time
Tubes Not Protected				
28.5 ng	26.5 ng	93%	24 l	10 min.
28.5 ng	19.0 ng	67%	48 l	30 min.
28.5 ng	5.0 ng	18%	143 l	60 min.
Protected Tubes				
28.5 ng	30.0 ng	105%	71 l	30 min.
28.5 ng	28.5 ng	100%	71 l	30 min.
28.5 ng	28.5 ng	100%	71 l	30 min.
38 ng	32.5 ng	86%	79 l	33 min.

Sulfur Loading by Filter Collection Techniques

The filter collection techniques employed at Cedar Island involved the dichotomous sampler and tandem filter packs. The dichotomous sampler divides the sampled particles by inertial impaction so that two size fractions are developed: a fine and a coarse particle fraction. The sampler is described in detail by Loo, et al (11). The tandem filter technique is used to collect size ranges (2) and can collect H_2S and SO_2 if specially coated filters are added. The adaptation of the technique for H_2S and SO_2 collection is the result of work done by Shaw (3).

The Dichotomous Sampler

A manual dichotomous sampler (12) was put into operation from August 23 to August 29 and run for 24-hour intervals starting at noon. The sampler was about 30 yards from the blockhouse and in a grassy area. The flow rate was 14 l/min. The filters used for both the fine and the coarse particle fractions were Millipore FALP (Teflon). The filters were weighed before and after exposure to determine the total suspended particulate. An x-ray fluorescence spectrometer (12) was used to analyze the elemental composition of the particulate collected on the filters.

The Tandem Filter Pack

The tandem filter pack (TFP) consists of a series of filters, each one of which extracts a component of the air stream passing through it. An exploded view of the TFP holder and filter assembly is shown in Figure 10. For the CIFS the first two filters in line (12 μm and 1 μm pore diameter Nuclepore) removed coarse and fine particles, respectively. The next filter removed SO_2, and the fourth and last H_2S. The gas collection filters were Millipore, FALP (Teflon) which supported thin layers of triethanolamine ($N(CH_2CH_2OH)_3$), isopropanol ($CH_3CHOHCH_3$),and water, mixed with sodium hydroxide (NaOH) for collection of SO_2 and copper nitrate ($Cu(NO_3)_2$) for H_2S. The SO_2 and H_2S filters were subsequently analyzed for sulfur by x-ray fluorescence. The x-ray fluorescence analysis system used by AIB has a sensitivity to sulfur such that 1 microgram can be detected at a confidence level of 90%. This corresponds to the sulfur loading obtained by sampling 1 ppb of either SO_2 or H_2S at 1 l/min for 12 hours. The absolute sulfur determination efficiency (collection efficiency times x-ray analysis efficiency) has been shown to be 60% $\pm$ 10% for both H_2S and SO_2 at relative humidities above 50% and at 20°C. An exploded view of the TFP holder and filter assembly is shown in Figure 10.

The sampling rate was set at 1 l/min and samples were taken over 24-hour intervals. Two sampling units were used: one remained near the block-house about 10 yards from the dichotomous sampler, the other was used in those areas where bag and chamber samples were taken.

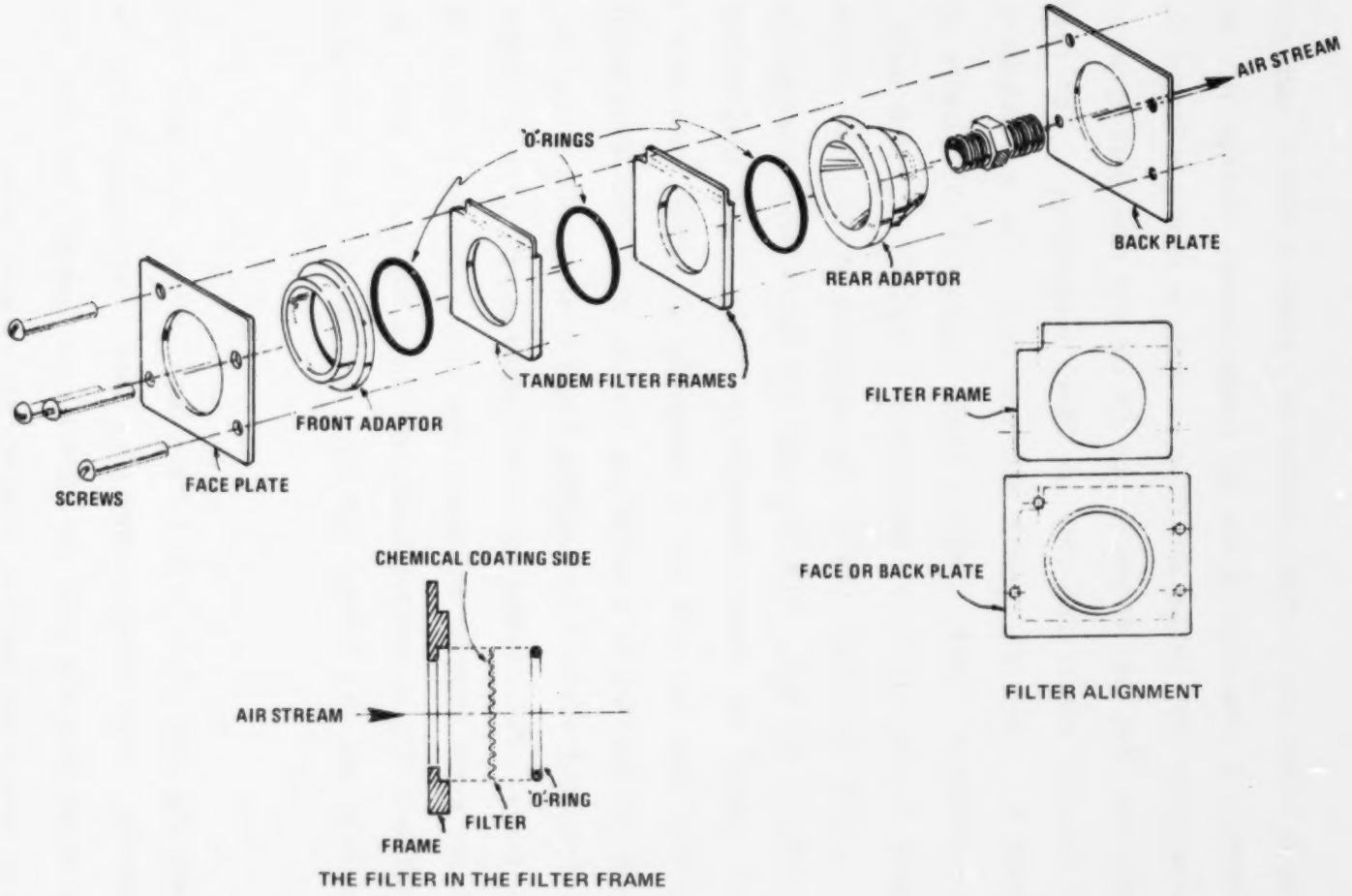

Figure 10. Holder and filter assembly for Tandem Filter Pack. Only two filter frames are shown although four filters were used in the CIFS experiments.

BIOGENIC RELEASE OF SULFUR IN GASEOUS FORM

Introduction

Biogenically released sulfur near the Cedar Island site contributes to the sulfur loading measured on the Island depending on wind direction and emission rates. An attempt was made to measure the biogenic sulfur released by the nearby marsh and to relate the sulfur compound mix to the compounds measured with the preconcentration techniques.

The problem of measuring biogenic sulfur release is complicated by the fact that local environmental conditions affect biogenic activity and make the assignment of emission rates and mix of emitted species based on localized measurements questionable. The investigators consider the results presented in this report as relevant only to the area in which they were obtained.

Environmental Chambers

Efforts to measure biogenic release from the Cedar Island marsh were centered on the use of an environmental chamber. The chambers used in the CIFS were enclosures which isolated a small area of ground so that gases released biogenically were prevented from rapid dispersion by prevalent winds and could be channeled into sampling bags for subsequent analysis.

Description of Environmental Chambers

The environmental chambers were similar to those described by Aneja (13). However, to avoid cutting the grass over certain of the monitoring sites, the air stirrer was detached. Figure 11 shows the chamber that was used during the studies. The chamber frame is just a modified office-type trash can. Windows were cut in the sides and top so that radiation could enter. Teflon sheeting was attached to the inside so that the Teflon surface and the area of ground covered by the chamber constituted an air-tight system. Ambient air was continuously pulled through the chamber from a small 1/4 in inlet in the lower section, and left the chamber from a similar connection near the chamber top. The accessory equipment shown in Figure 11 includes a pair of 12 volt batteries in series to power the air pump (Brailsford, Model TD4X2) which is mounted on the rim of the chamber. Flow rates through the air pump were periodically checked with a mass flow meter (Sierra Instruments, Model 543). Soil and ambient temperatures were measured with a thermister made by Yellow Springs (Model 46 TUC).

To sample the air passed through the chamber, a Teflon bag was attached to the pump outlet with a Teflon tube. The bag was filled and then transported to the blockhouse site where they were placed outside the blockhouse in the sunlight to prevent condensation of H_2O. During analysis a Teflon line was run from the bag, through a window into the blockhouse, to a Meloy, Model SA 285, for analysis. An SO_2 scrubber

Figure 11. Environmental chamber for measurement of biogenic emissions.

Figure 12. Monitoring site B. Marsh adjacent to Lewis Creek.

made by Meloy was usually heated and placed in the sample line so that the readings were total sulfur minus SO_2.

Sample integrity was of primary concern in the chamber experiments. Losses of H_2S and $(CH_3)_2S$ in the Teflon bags were measured during the field study at 15% per hour and 5% per hour, respectively. These loss rates were determined by putting known amounts of the two gases in bags and taking two readings, an initial reading and a second reading after 3 hours. Dry air was used in the tests. Bag losses as well as memory effects were of concern. In this regard, it was found that the bags had to be flushed three times before a zero response could be observed on the Meloy sulfur monitor. Continual inspection of the bags for leaks was necessary to avoid spurious results.

Placement of Chambers

Chambers were placed in several locations for limited periods of time (typically half-day periods) and in two locations for continual analysis during 2-day periods. Order of magnitude variations in chamber concentrations were observed from location to location, diurnal and tidal-related variations were observed during the long term analyses.

The primary location for chamber studies is denoted as Site A in Figure 1. Site A is along the edge of Lewis Creek. In this area intertidal edgewater locations were chosen. The majority of the edgewater area (Site

A-1) was overgrown with a type of marsh grass -- Spartina alterniflora -- and interlaced with seaweeds held in place by the stem and root systems of the marsh grass. The soil was a mixture of silt and sand, tan to dark brown in color. Site A-2 was located near a docking area which fronted on Lewis Creek. This area was sandy with little grass or seaweeds.

Site B, as shown in Figure 12, is in the marsh adjacent to Lewis Creek. It was selected as being more representative of the marsh area than Site A (see Figure 13). Site C was chosen as representative of the intertidal flats that border the sound side of the Outer Banks. These flats are shown in Figure 14.

Calculation of Generation Rates

The assumption of ideal mixing in the environmental chamber establishes the following relationship: the rate of release "R" of a sulfur compound of gram molecular weight "G" from the area "A" covered by the chamber is related to the flow rate "F" through the chamber and concentration at the outlet "f". The equation goes as follows:

$$R(gm/m^2\text{-}yr) = \frac{f(ppb)}{A\ (m^2)}\ F(l/min)\ \frac{G(gm/mole)}{K\ (l\text{-}atm/mole\text{-}deg)}\ \frac{P(atm)}{T(deg)}\ C(min/yr), \quad \text{(Eq. 2)}$$

where $C = 5.256 \times 10^5$, $A = 0.085\ m^2$ for the chamber used in the CIFS, G = 62 for $(CH_3)_2S$ and G = 34 for H_2S, and K = 0.082 l-atm/mole-deg. P

Figure 13. Monitoring site A. Intertidal edgewater location near blockhouse on Cedar Island.

Figure 14. Monitoring site C. Interdial flats on Outer Banks.

is the atmospheric pressure and T the ambient temperature. Note that for a constant generation rate the value of concentration is inversely proportional to the flow rate, i.e., $f(ppb) \sim [F(\ell/min)]^{-1}$.

Equation 2 must be interpreted with care if it is to be used to estimate the biogenic flux which would occur in the absence of an environmental chamber. The main questions associated with the use of chambers concern (a) the perturbation of the environment being monitored by the chamber, e.g., the possibility of temperature and humidity changes within the chamber; (b) the effect of increased partial pressures of the gases to be measured over the area enclosed by the chamber; (c) the degree of stirring required in the chamber; and (d) the tightness of the air seal around the chamber. In the present case, ambient air was pulled through the chamber so that humidity changes were minimized; however, an increase in temperature was evident from the water condensation on the chamber walls. The questions (b) and (c) above are discussed in some detail by Hill, et al. (14). In the CIFS, sampling was performed over grass, so that the chamber could not be stirred. Item d is important when the sample air is being pulled through the chamber. In this case a check should be made to determine if the flow rate entering the chamber and that leaving the chamber are equal. To measure the combination of the effects mentioned in (b) (c) and (d), the chamber concentrations were recorded as the chamber flow rate was varied. The departure of the

results from that given in Equation 2, i.e., f ~ 1/F, was taken as an empirical determination of the applicability of Equation 2. The result of this determination is given in Results and Discussion.

ATMOSPHERIC BACKGROUND MEASUREMENTS OF NITROUS OXIDE, FREON 11, AND FREON 12

As part of the CIFS, five ambient samples were taken for subsequent analysis to determine N_2O, Freon 11 and Freon 12 content. The five samples were all taken at the same time on September 1 and at the same place (height of 7 m); they were expected to be replicates. The containers were returned to RTP for subsequent analysis on November 8. Due to the significant delay in analysis any differences in the results of the separate container samples were expected to reflect the compromise of sample integrity attendant to storage. The results were expected to illustrate AIB's capability to analyze samples for N_2O, Freon 11 and Freon 12 with a set of optimized gas chromatographic columns, and to provide estimates of sample integrity after storage in sampling containers.

Development of better and more convenient analysis techniques seem especially appropriate in the case of N_2O, since it has been suggested that the N_20 level is constant and could be used as a reference to check analytical instrument performance. The concentration levels reported, however, have ranged from 0.25 ppm in 1974 to 0.32 ppm at the present time. It is not clear whether this increase is due to a refinement in the

measurement technique of a constant concentration level, or whether N_2O levels are on the increase in the atmosphere.

Accurate measurement of N_2O, Freon 11 and Freon 12 is extremely important since their presence in the atmosphere contributes to the greenhouse effect -- the blanketing action which leads to an increase in the earth surface temperature (15).

Measurement Techniques

Gas chromatography with electron capture detection was used to determine the Freons and N_2O. The analytical system was comprised of a Barber-Coleman Series 5000 Gas Chromatograph, an Analog Technology Corp. Model 140 Detector, and a Carle 8-Port Sampling Valve with a 6-ml loop and a Hewlett-Packard Model 3385 A Integrator. The halocarbon and N_2O analyses were done on separate columns.

Conditions for the determination of Freon 11 and Freon 12 were:

- Column: 7 ft x 1/8 in Porasil C, 80/100 mesh;
- Column Temp: Ambient;
- Carrier: 5% methane in argon;
- Flow rate: 41 ml/min at 22 psig;
- Detector temp: 190°C.

The conditions for the determination of N_2O were:

- Column: 8 ft x 1/8 in Porapak Q, 80/100 mesh;
- Column Temp: Ambient;
- Carrier: 5% methane in argone;
- Flow rate: 32 ml/min at 25 psig;
- Detector temp: 190°C.

A cursory study indicated that one analytical column, packed with Chromosil 310, can be used for the determination of the above three components. The column unfortunately was not ready for this project. It will be used for such analyses in the future.

Calibration of the system consisted of recording responses to reference mixtures. These reference mixtures (one component per container) were composed in stainless steel cylinders by a method of static pressures.

Evacuated containers were used for sampling: four steel containers (800 cc each) and one stainless steel cylinder (500 cc). Each container had been outgassed by heating and pumped down to a pressure of 20 μm prior to use.

The containers were heated to 80°C in a drying oven in the laboratory just prior to analysis in order to increase container pressure to

about 21% above collection pressure. This maneuver provided two samples per container.

ATMOSPHERIC MEASUREMENTS OF OZONE AND NITROGEN OXIDES

Ozone measurements at Cedar Island were expected to show some correlation with ambient sulfur levels due to the H_2S - O_3 gas phase reaction. Also, the availability of two types of O_3 measuring instruments - one based on 0_3 - C_2H_4 chemiluminiscence and the other on ultraviolet (UV) photometry -- made possible a comparison of techniques.

Measurements of NO_x were used as an indication of the isolation of the Cedar Island site. In addition a new commercial monitor, the CSI Series 1600, was tested for sensitivity and reliability under field conditions.

Measurement Apparatus

The O_3 instrumentation, Dasibi, Model 1003-AH, and Bendix, Model 8002, are established commercial instrumentation. The Dasibi is based on UV photometry and a chemical scrubber system for O_3. In operation the sample stream either bypasses or passes through an O_3 scrubber and is subsequently analyzed by the measuring attenuation difference at 2537 Å. The Bendix instrument causes mixing of the sample stream with a pure stream of C_2H_4. The reaction of O_3 with C_2H_4 occurs with an attendant

emission of photons. Photon emission as monitored on a photomultiplier gives a signal proportional to the concentration of O_3 in the sample stream.

Measurement of Ozone and Nitrogen Oxide

Ozone and NO_x were monitored from a common manifold in the mobile van. The sample inlet line of 1/4 in ID Teflon tubing contained an in-line Nuclepore filter of 5 μm pore diameter. Both O_3 monitors (Dasibi and Bendix) as well as the CSI NO_x monitor were operated continuously.

Calibration of Ozone and Nitrogen Oxides

The O_3 and NO_x calibrations are estimated to be better than ± 20% for the two week measurement period.

The O_3 calibration was based on UV absorption photometry. The Dasibi (Serial No. 1237) and Bendix (Serial No. 302070-2) monitors were calibrated at RTP prior to the field study. During the study the Dasibi experienced an obvious intermittent electronic malfunction which allowed only about 70% valid data from the instrument. During the periods when the Dasibi was functioning properly the Bendix and the Dasibi tracked each other within ± 10% except for a brief period following excessive condensation of ambient water in the sample lines. After returning the instruments to RTP, the Dasibi did not function. The Bendix calibration

was checked by the gas phase titration apparatus (GPT) and was found to be approximately 3% high. Since 3% is less than the typical difference between GPT and UV O_3 calibration, the instrument drift was considered to be negligible (i.e. <5%).

The NO_x calibration was based on an NO cylinder (the cylinder concentration was determined by comparison to an Standard Reference Material (SRM) cylinder via GPT. Immediately prior to the field trip the NO_x instrument (CSI, Model 1600, Serial No. 8195) was returned to the factory for repairs and calibration. The calibration was checked at RTP prior to the trip and was found to be within 2% of the factory value. Similarly the converter efficiency was found to be within 1% of the factory value ($\simeq$ 98%). After the field study the instrument was returned to RTP and the NO calibration was found to be $\simeq$ 6% lower. The converter efficiency was not rechecked at RTP.

During the field study several attempts were made to check the instrument calibration via GPT. None of these efforts produced results within 30% of the instrument's response. Upon later examination of the GPT system it appeared that the most likely cause for the field calibration results was improper purging of the NO tank regulator. (The regulator was removed from the tank during transportation both to and from the field study site.) Because of the large deviation between the field calibration results and the instrument response, no adjustments to the instrument spans were made in the field.

SECTION 3

RESULTS AND DISCUSSION

GASEOUS SULFUR COMPOUNDS IN AMBIENT AIR

Direct Measurements Using Flame Photometric Detection

Direct readings of ambient gaseous sulfur with the Meloy SA 285 were taken during the first part of the field test. Total sulfur-sulfur dioxide levels were always below 5 ppb. Due to the difficulty in distinguishing values below 5 ppb with precision, the direct measurements were discontinued.

Preconcentration on Gold-Coated Glass Beads

Several types of sampling studies were planned, including: sampling of air coming from the ocean, sampling as a function of height above the ground (tower studies), sampling and analysis as a function of time (diurnal variations), sampling of biogenic emissions, and sampling in support of other investigators. Each study was performed to some

degree; however the time variation study could not be carried out over more than a few hours because of difficulties in maintaining the sampling tubes in a suitably blank condition. The placement of local vegetation and wind direction appeared to have a substantial influence on the sulfur analyses obtained.

Tower Studies

Air samples were obtained using a 10 meter high mast which could be raised and lowered to attach sampling tubes and fittings. Small vacuum pumps (Neptune Dyna-Pumps, Fisher Scientific Co.) were placed at the foot of the towers and connected at various heights to the sampling tubes by tygon tubing. Tower samples were taken at 10, 5, 2, 1, and 0.1 meters. Also available was an abandoned radar antenna tower from which 20 meter high samples could be taken. Five 10-meter tower sample sets were taken in the course of the field work. Figure 15 depicts the various tower study sites on Cedar Island. Figure 16 shows typical chart recordings from the gold bead analysis. The label "RS" refers to the unseparated sulfur compounds in the sample released from the cold trap into the Meloy.

The distribution of reduced forms of sulfur is given in Table 5, A-F, and shown in Figures 17-21 as a function of height above the ground. Towers 1 and 2 were taken at a location as close as practical to the edge of the sound. There were no mud flats at this location. Notable are the

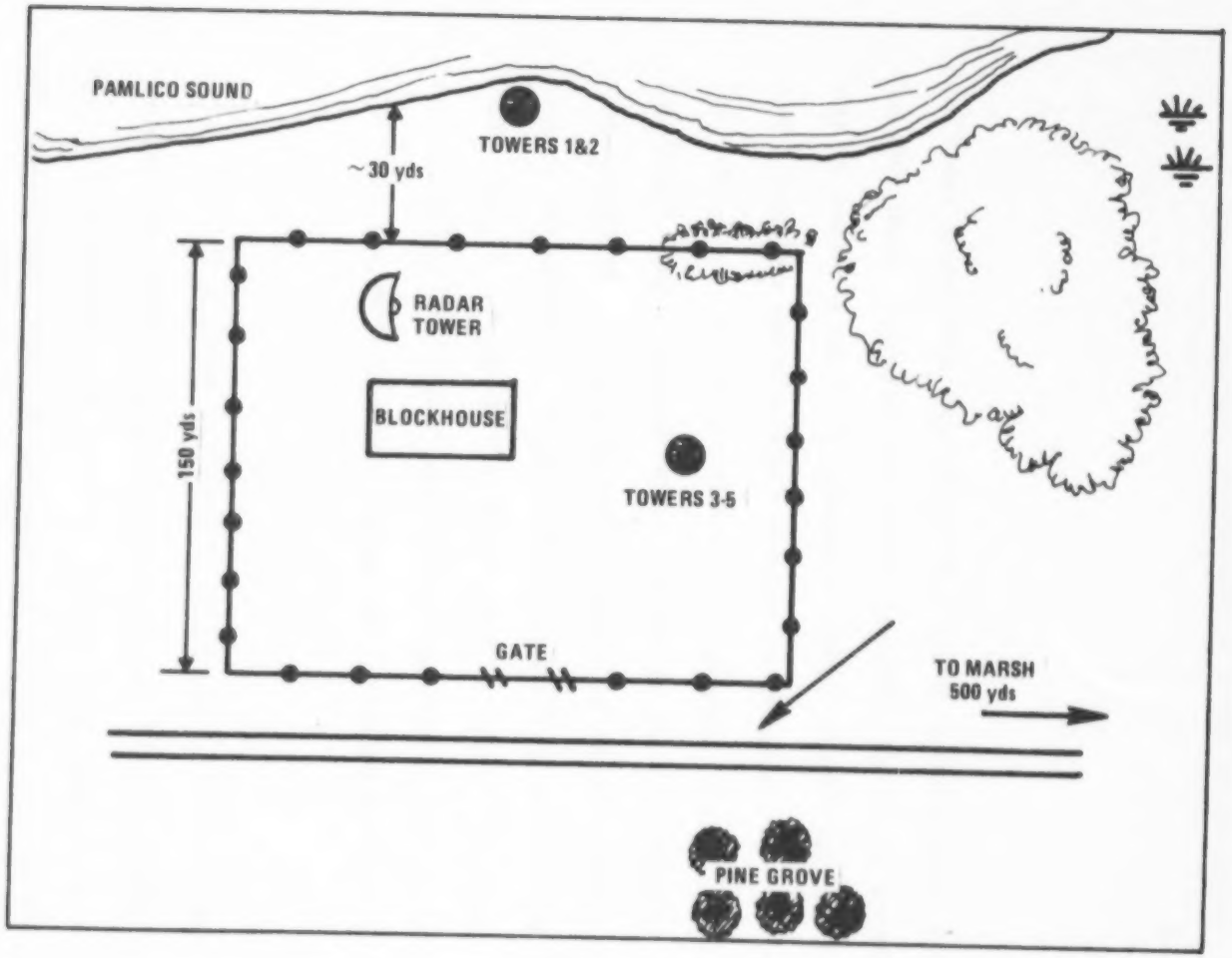

Figure 15. Tower study sites near Cedar Island blockhouse.

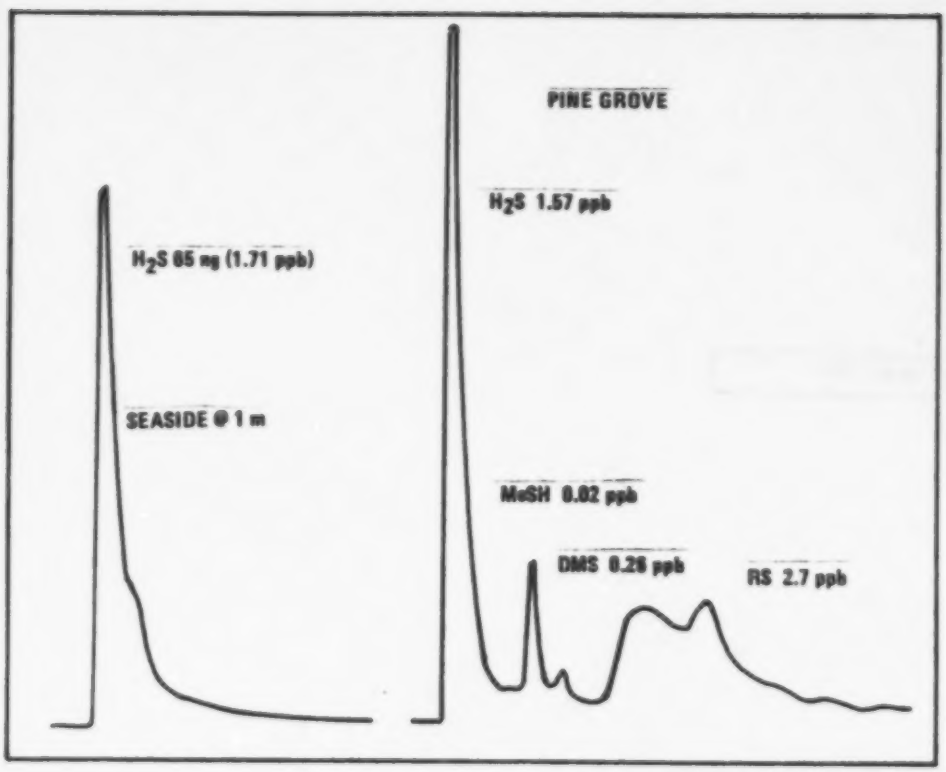

Figure 16. Typical chart recordings from the gold-coated glass bead analysis.

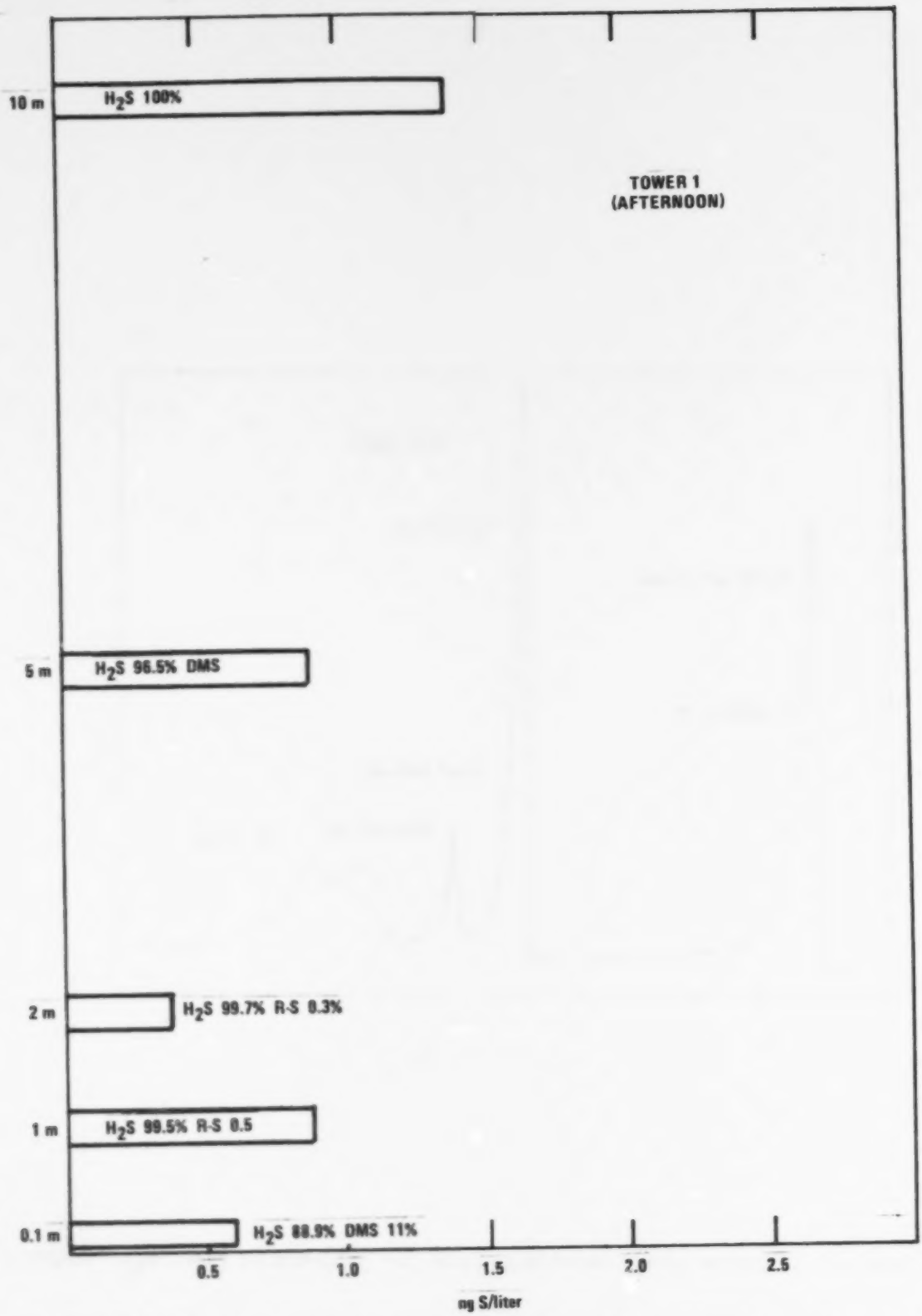

Figure 17. Vertical concentration profiles of sulfur compounds -- Tower 1

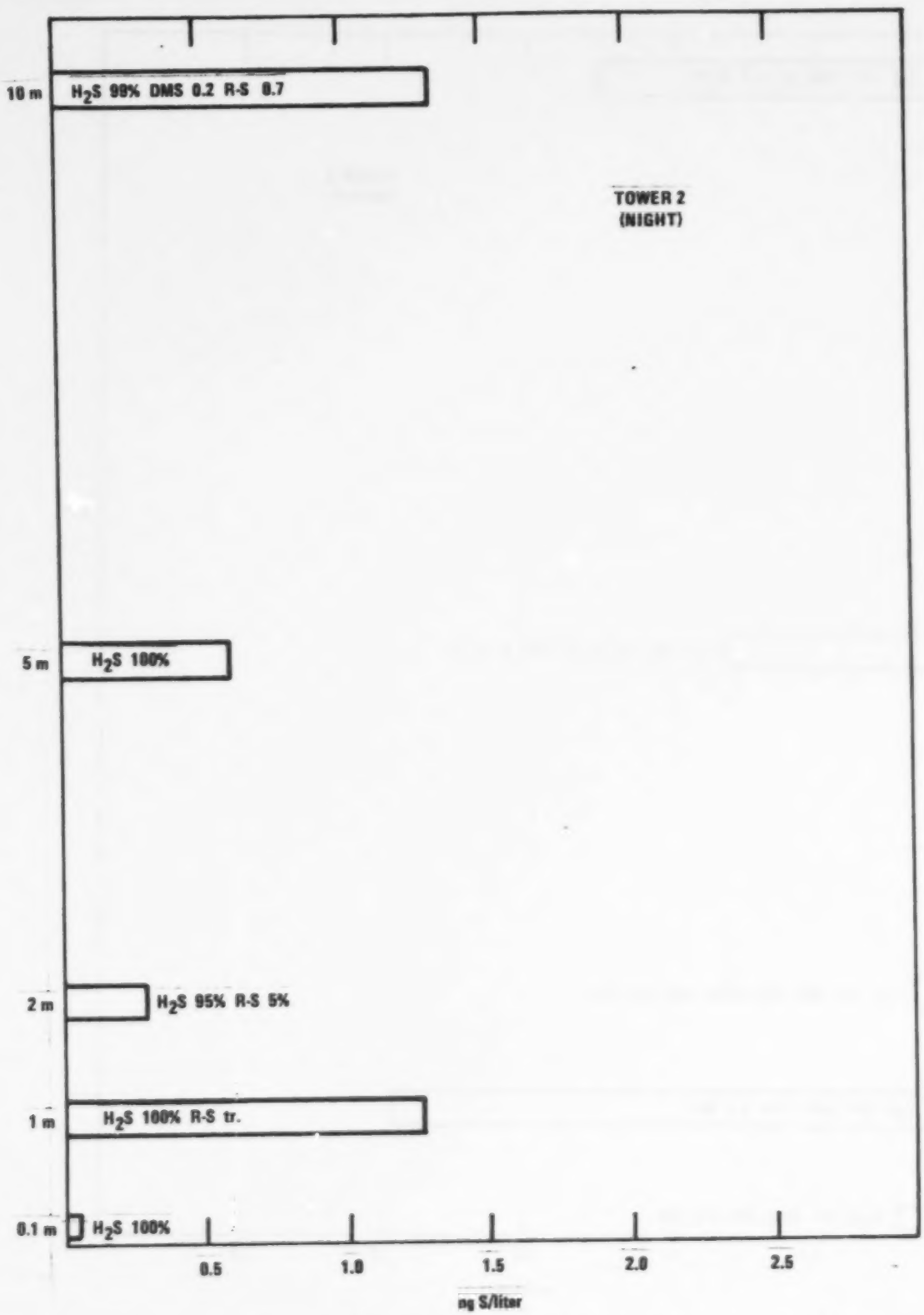

Figure 18. Vertical concentration profiles of sulfur compounds -- Tower 2.

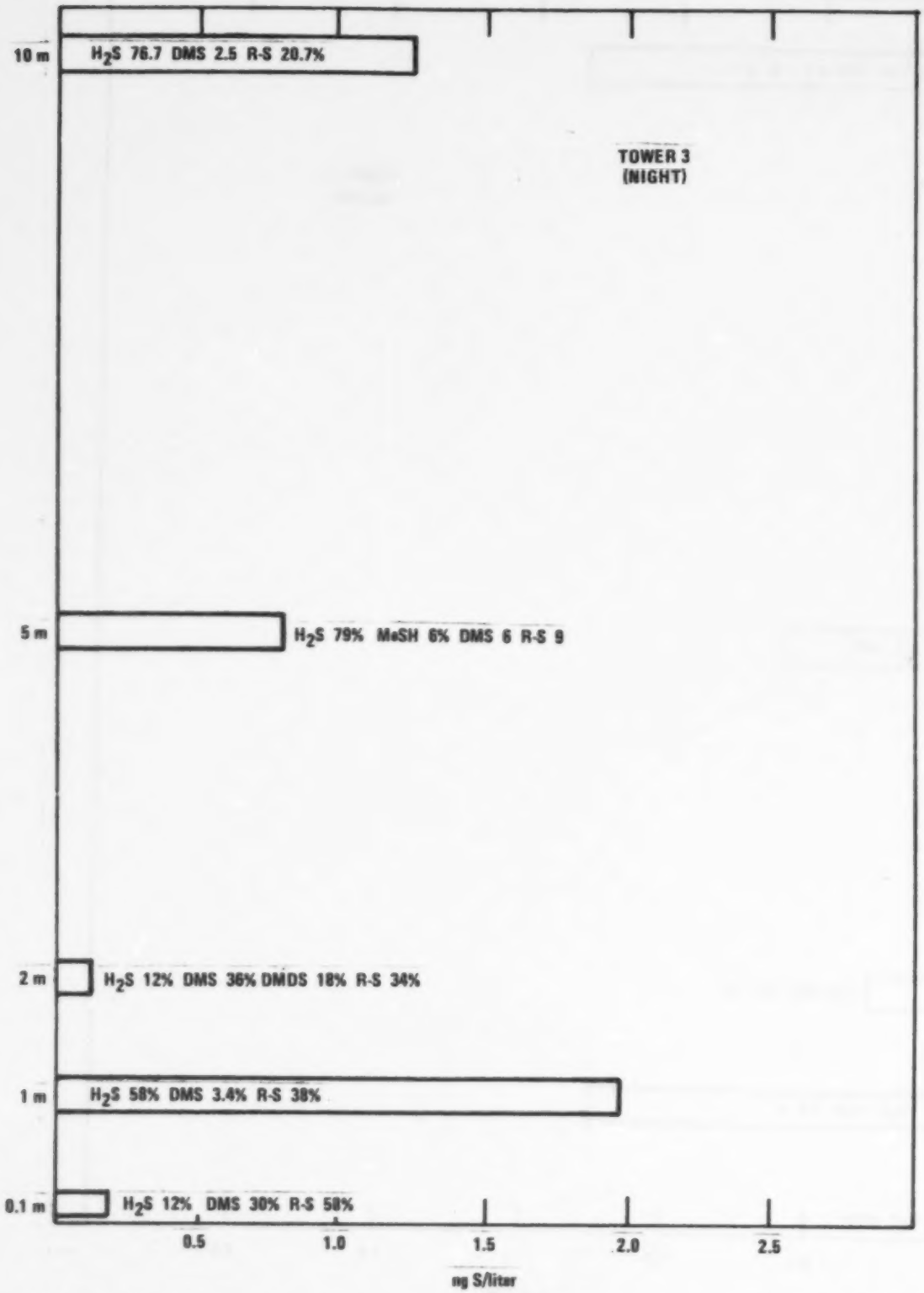

Figure 19. Tower 3. Vertical concentration profiles of sulfur compounds.

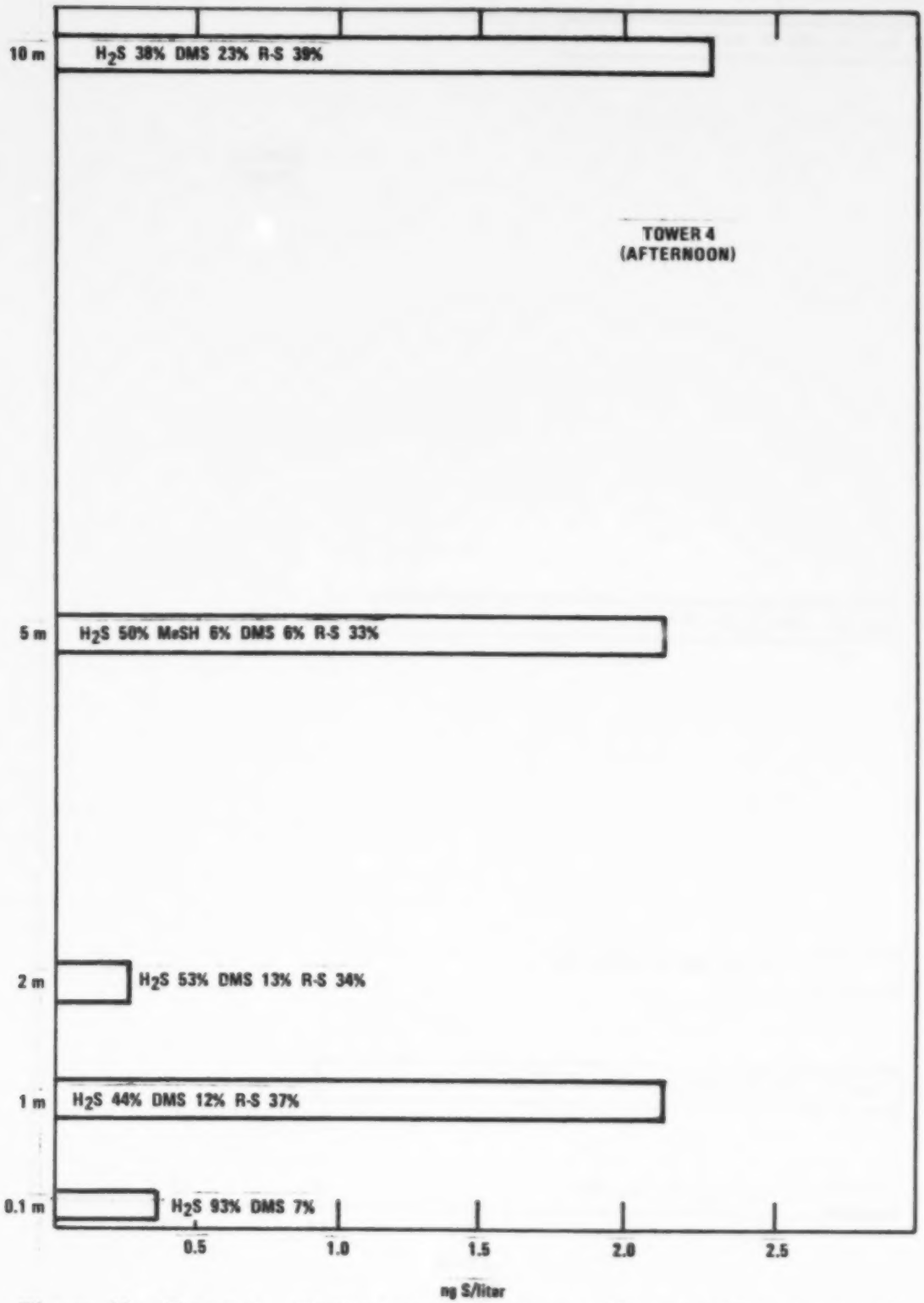

Figure 20. Tower 4. Vertical concentration profiles of sulfur compounds.

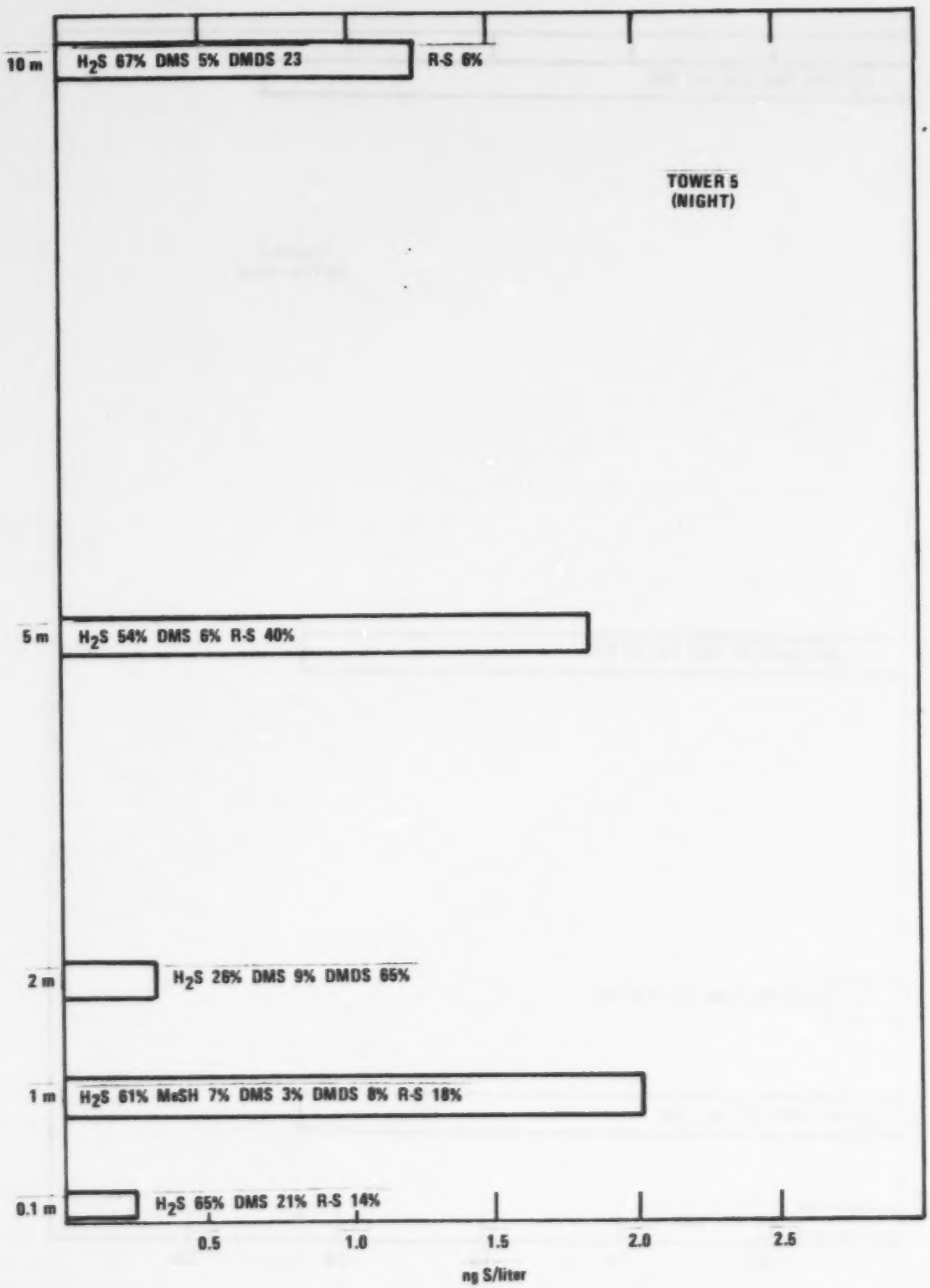

Figure 21. Tower 5. Vertical concentration profiles of sulfur compounds.

high percentage of H_2S and the low percentage of other reduced forms of sulfur. Towers 3-5 were taken in the open field near the blockhouse with wind directions generally from the marsh area. All of these had a substantially higher organosulfur compound content than those taken near the sound.

A regular pattern of sulfur concentration was noted in most of the tower studies with a maximum at 1 meter and with total reduced sulfur concentrations increasing with the height above ground. Since the maximum in concentration at 1.0 meters does not appear to be consistent with either a dry deposition or biogenic emission of the sulfur gases, the experiment must be repeated to judge whether this maximum is an artifact introduced by the sampling train or is due to the micrometeorology of the surrounding area. In any case the vertical variation points out the problem of picking a representative vertical position for ambient air sampling. Sampling at 10 meters was more indicative of an average sulfur value; organosulfur compounds were very low at 2 meters, the usual height for meteorological sampling.

Samples were taken from the radar tower located near the blockhouse at a height above ground of approximately 20 meters. Results of analyses are given in Table 6. Hydrogen sulfide was the major reduced sulfur component in most cases. Very little contribution was noted from organosulfur compounds. Some of the 20-meter samples were taken at the

same time as the 10-meter tower studies. Comparison of the 20-meter and 10-meter tower samples, where feasible, shows substantial agreement in composition and, generally, in the concentration of the reduced sulfur compounds found.

A number of miscellaneous samples were taken with data given in Table 7. These data include analysis of samples taken from several sites: Site A, Site B, and Site C, as well as samples taken in the area of a pine grove, and two measurements taken at Cox's Landing, North Carolina.

Discussion of Results Obtained Using Gold Coated Glass Bead Preconcentrator

A comparison of ocean air samples to on-shore samples was made (see Table 8). Ocean air samples were defined as air samples taken near the waters' edge with wind from the ocean direction. On-shore samples were defined as samples taken further inland with wind generally from the land direction. On-shore samples and the pine grove samples all contained much higher amounts of organosulfur compounds. This agrees with Rasmussen's comments (15), that a number of different organosulfur compounds are associated with biological sources.

During the development of the analytical method, the major objective was to provide a method principally for H_2S, CH_3SH, and $(CH_3)_2S$; these were satisfactorily separated in the U-trap. However, a much more complex mixture of sulfur compounds was found (See Figure 16) and the

unseparated, less volatile organosulfur compounds had to be reported as a group. An improved separation method is now under study.

A gas chromatographic type of FPD air analyzer was in use during the sampling of ambient air. Hydrogen sulfide was detected in ambient air at concentrations in agreement with the preconcentration method described here. Sulfur dioxide was detected at levels less than 5 ppb. Consequently, the SO_2 capacity of the scrubber tubes was not approached during sampling.

The method has certain limitations. The sulfur compounds carbon disulfide ($CS_{2)}$ and COS are interferents, since both appear as H_2S after absorption on the gold tubes and after hydrogen reduction. Although some of these are removed by the SO_2 scrubbing traps, an improved separation technique is needed. In addition, some decomposition of mercaptans to H_2S was noted during hydrogen reduction and was generally a function of the total amount present. No decomposition of $(CH_3)_2S$ was observed.

Finally, the method does have the capability of providing analytical information on H_2S and $(CH_3)_2S$ found in air at ambient concentrations in non-polluted locations. It should substantially aid studies of the environmental chemistry of sulfur.

TABLE 5. TOWER SAMPLE DATA

A. Tower 1

(8-24-77, 1650-1720 hr, 70-90 l)

Height m	H_2S ppb	H_2S ng/l	$(CH_3)_2S$ ppb	$(CH_3)_2S$ ng/l	RS ng/l as H_2S
10	0.94	1.46	0.00	tr.	0.00
5	0.59	0.90	0.02	0.06	0.001
2	0.26	0.40	0.00	0.00	0.00
1	0.6	0.93	0.00	0.00	0.004
0.1	0.24	0.37	0.03	0.08	0.00

B. Tower 2

(8-25-77, 2140-2230 hr, 90-109 l)

10	0.90	1.38	0.002	0.006	0.011
5	0.41	0.63	0.00	0.00	0.00
2	0.19	0.29	0.00	0.00	0.015
1	0.88	1.35	0.00	0.00	0.001
0.1	0.02	0.03	0.00	0.00	0.00

(continued)

TABLE 5. (Continued)

C. Tower 3

(8-27-77, 2000-2030 hr, 67-90 l)

10	0.70	1.03	0.24	0.062	0.28
5	0.71	1.04	0.036	0.095	0.07
2	0.01	0.01	0.28	0.73	0.037
1	0.80	1.23	0.050	0.13	0.81
0.1	0.015	0.02	0.038	0.10	0.11

D. Tower 4

(8-28-77, 1550-1650 hr, 40 l)

10	0.60	0.93	0.40	1.04	0.95
5[a]	0.73	1.13	0.092	0.24	0.88
2	0.097	0.15	0.025	0.065	0.098
1	0.65	1.58	0.19	0.49	0.99
0.1	0.23	0.35	0.017	0.045	0.00

(continued)

TABLE 5. (Continued)

E. Tower 5 (8-28-77, 2000-2100 hr, 40 l)					
10[a]	0.58	0.90	0.046	0.12	0.78
5	0.69	1.06	0.084	0.22	0.80
2[c]	0.058	0.09	0.021	0.055	0.00
1[d]	0.86	1.33	0.038	0.10	0.48
0.1	0.11	0.16	0.036	0.095	0.04

[a] CH_3SH: 0.20 ng/l
[b] $(CH_3)_2S_2$: 0.15 ng/l as H_2S
[c] $(CH_3)_2S_2$: 0.11 ng/l as H_2S
[d] $(CH_3)_2S_2$: 0.09 ng/l as H_2S; CH_3SH: 0.21 ng/l

TABLE 6. TOWER SAMPLES AT 20 METERS

Date	Time of Day	H_2S ppb	H_2S ng/l
8-27-77	1200-1300 hr	0.00	0.00
8-27-77	1305-1425 hr	0.29	0.45
8-27-77	1425-1550 hr	0.10	0.16
8-27-77	1550-1715 hr	0.23	0.36
8-27-77[a]	2030-2130 hr	0.20	0.30
8-28-77	1610-1710 hr	0.94	1.45
8-28-77[b]	1715-1816 hr	0.53	0.81

[a] $(CH_3)_2S$: 0.03 ng/l 0.01 ppb; $(CH_3)_2S_2$: 0.02 ng/l as H_2S
[b] $(CH_3)_2S$: 0.22 ng/l 0.08 ppb CH_3SH: 0.02 ng/l

TABLE 7. MISCELLANEOUS SAMPLES

Time	Location	H_2S ppb	H_2S $\mu g/m^3$	Others
		A. Cox's Landing, North Carolina		
8-29-77 Evening		9.3	14.3	$(CH_3)_2S$: 0.1 ppb, $(CH_{32}S_2$: 0.25 ppb as H_2S
		11.4	17.6	$(CH_3)_2S$: 0.1 ppb, $(CH_3)_2S_2$: 0.08 ppb as H_2S
		B. Cedar Island, North Carolina		
8-22-77 1240 hr	Seaside Edge	0.28	0.43	$(CH_3)_2S$ 0.038 ng/l
8-22-77 1050 hr	Seaside Edge	1.71	2.64	-------
8-23-77 1130 hr	Site 3, 2 ft	3.57	5.5	-------
8-23-77 1110 hr	Site 3, 1 ft above ground	1.69	2.6	
8-23-77 1250 hr	Site 2, 2 ft above water	0.10	0.15	$(CH_3)S$: 0.034 ng/l; RS: 0.36 ng/l as H_2S
8-23-77 1200 hr	Site 4, J. Day's Ditch	0.08	0.12	-------

TABLE 7. (Continued)

Time	Location	H_2S ppb	H_2S ng/l	Others
		B. Cedar Island, North Carolina		
8-23-77 1230 hr	Bag sample 1	1.04	1.60	$(CH_3)_2S$: 7.6 ng/l, 2.9 ppb
8-23-77 1240 hr	Bag sample 2	0.68	1.05	-------
8-23-77 2245 hr	Blockhouse near fence	0.24	0.37	$(CH_3)_2S$: 0.009 ng/l, 0.003 ppb
8-26-77 (AM)	Boat landing	0.38	0.59	-------
8-26-77 1200 hr	Boat landing	1.25	1.93	-------
8-26-77 1630 hr	Seaside Edge	0.15	0.23	$(CH_3)_2S$: 0.10 gn/l, 0.038 ppb
8-27-77 1830-1910 hr	Drum Inlet	0.88	1.36	

TABLE 7. (Continued)

Time	Location	H_2S ppb	H_2S ng/l	Others
		B. Cedar Island, North Carolina		
8-28-77 1100 hr	Chamber No. 2	3.4	5.24	$(CH_3)_2S$: 33 ng/l, 15.6 ppb, RS 8.3 ng/l as H_2S
8-28-77 1700 hr	Chamber No. 1	32.0	49.3	$(CH_3)_2S$: 68.4 ng/l, 26.1 ppb
8-29-77 925 hr	Pine Grove	1.57	2.42	$(CH_3)_2S$: 0.40 ng/l, 0.15 ppb; CH_3SH: 0.05 ng/l RS: 2.7 ng/l as H_2S
8-29-77 925 hr	Pine Grove	0.96	1.48	$(CH_3)_2S$. 0.03 ng/l 0.01 pp; RS 0.71 ng/l as H_2S

TABLE 8. PERCENTAGE COMPOSITION OF REDUCED FORMS OF SULFUR

Ocean Air Samples			
Towers	No. 1	H_2S	96.9 ± 4.7% n = 5
	No. 2	H_2S	98.8 ± 2.2% n = 5
Seaside	1 m	H_2S	99.5 ± 3.6% n = 5
Radar Tower	20 m	H_2S	96.1 ± 6.2% n = 4
On-Shore Samples			
Towers	17 Samples		
		H_2S	53.2 ± 23%
		CH_3SH	1.2%
		$(CH_3)_2S$	12.1%
		$(CH_3)_2S_2$	7.9%
		RS	25.34%

Tandem Filter Measurements

Results for the sulfur measurements in SO_2 and H_2S are shown in Figure 22. With the exception of one measurement for SO_2, all values were less than 1 $\mu g/m^3$. These results are consistent with the generally low values determined via the gold-coated glass beads, but a close comparison is difficult because the TFP and gold bead sampling times are 24 and 1/2 hours, respectively; and, as the previous attitude profiles show, the concentration of sulfur gases was strongly dependent on altitude, stressing the importance of the height of the sampler.

PARTICULATE MEASUREMENTS IN AMBIENT AIR

The Dichotomous Sampler

The ranges and mean values for individual elemental abundances as well as the total mass for the fine and coarse particle fractions are given in Tables 9 and 10. The values in Table 9 indicate that elements heavier than aluminum contribute about 2-3 $\mu g/m^3$ or 11-17% to total fine particulate mass. The remaining mass is likely to be adsorbed water and compounds of light elements (optical microscopy shows seed fragments on several of the fine particle filters). The principal element determined was sulfur

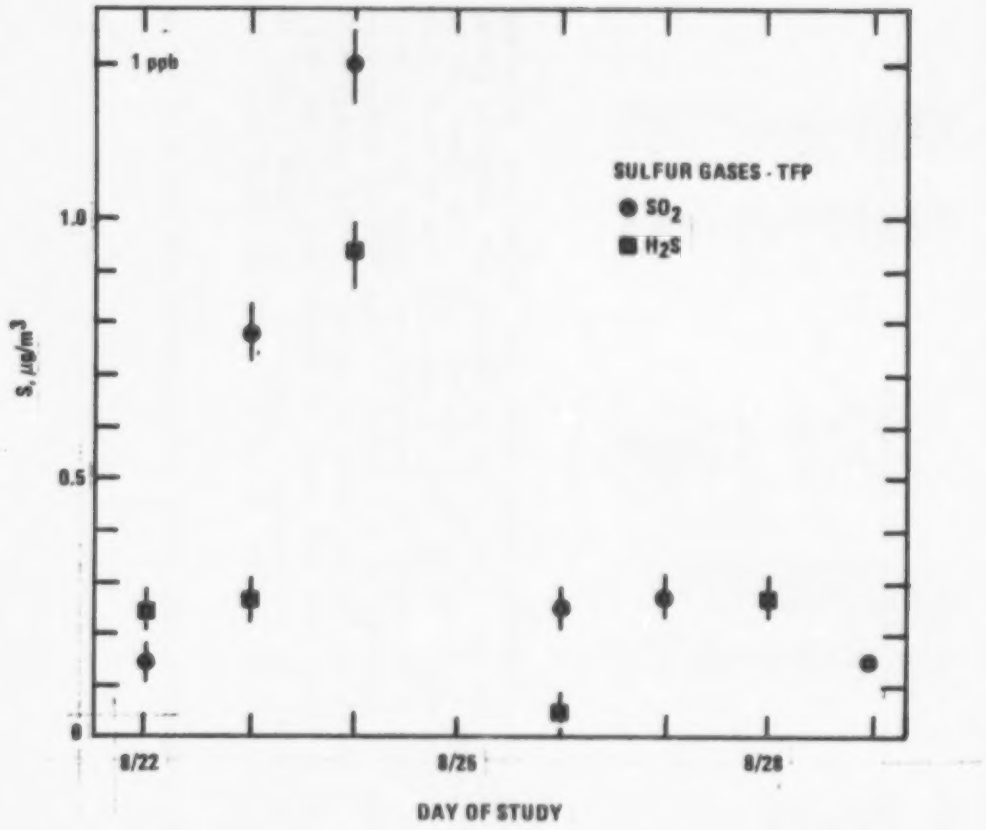

Figure 22. Sulfur dioxide and H_2S content of the ambient air using the TFP and x-ray fluroescence.

TABLE 9. FINE PARTICLES (ng/m^3)*

	Tandem Filter Pack		Dichotomous	
Element	Range	Mean+	Range	Mean
Al	<100-600	<270 (170)		<23 (23)
Si		<140 (140)	<10-51	<25 (19)
S	500-3000	1400 (800)	700-4500	2200 (1200)
Cl	<30-280	<160 (80)	<3-190	<50 (80)
K	<15-90	<50 (30)	<4-59	<30 (23)
Ca	<11-70	<40 (20)	<1-46	<22 (18)
Ti	<12-137	<80 (40)		<5 (5)
Fe		<17 (20)	<2-76	<27 (26)
Zn		<10 (11)	<3-14	<7 (4)
Br		<5 (5)	<1-9	<4 (3)
Pb	<9-76	<30 (20)	8-94	36 (29)
TSP $\mu g/m^3$			8-36	18 (9)

*In cases where an elemental abundance was below the minimum detectable level (MDL) for one or more measurements, the range is given as MDL - MV where MV is the maximum measured value. In these cases, the mean is an upper limit. If the MDL is exceeded for no more than one measurement, that measurement is neglected, no range is reported, and the mean MDL is reported as the "mean." The MDL is defined as follows: $MDL = 3.29 (R/t)^{\frac{1}{2}}/S$ in units of ng/cm^2. The background count rate, R, for a clean filter has units of counts/sec; t is the time; and S is the sensitivity in $(counts/sec)/(ng/cm^2)$. In Table 9 and 10 MDL has been converted fro ng/cm^2 to ng/m^3 using the filter area and sample volume.

+The uncertainty associated with x-ray flurorescence analysis is given in parentheses.

TABLE 10. COARSE PARTICLES (ng/m^3)*

	Tandem Filter Pack		Dichotomous	
Element	Range	Mean (SD)**	Range	Mean (SD)
Si	<3-190	72 (56)	<8-72	<23 (27)
S	70-310	200 (80)	<8-53	<41 (32)
Cl	140-1400	770 (500)	<3-79	<54 (49)
K	<20-120	<53 (33)	<1-11	<2 (4)
Ca	28-86	58 (21)	<1-30	<6 (11)
Fe	<11-237	<49 (77)	<2-42	<11 (15)
Ni		<7 (7)	<1-29	<6 (11)
Cn	<4-55	<16 (17)	<1-4	<2 (1)
Zn		<10	<1-18	<5 (7)
Br	<1-16	<9 (5)	0-3	<1 (1)
Sr	<1-12	<4 (4)	0-1	<1 (1)
TSP $\mu g/m^3$			4-82	28 (33)

*See footnotes to Table 4
**SD stands for Standard Deviation.

and the amount corresponds to a mean value as sulfate of 6.6 where the distribution of sulfate values about the mean exhibited a standard deviation of 3.6 $\mu g/m^3$. The total sulfate value measured by the National Air Surveillance Network for non-urban sites in 1974 was 6.2 with a standard deviation of 6.2 $\mu g/m^3$; these measurements were made by Hi Vol samplers which do not discriminate between coarse and fine particles.

Those elements in the coarse particle fraction which are above our MDL account for only 0.5% of the total mass. The surprising near-absence of the elements aluminum, silicon, calcium and iron which are usually associated with particles from the earth's crust and which often make up a major part of the coarse particles, indicates that the coarse particle orifice section of the dichotomous sampler may have been plugged during these experiments. On the other hand, the near absence of these particles in the coarse TFP fraction as well, suggests that the air sampled was, in fact, extraordinarily clean of coarse particles.

The Tandem Filter Pack

The elemental abundances for the TFP coarse and fine particle filters are found in Tables 9 and 10. Roughly speaking, the trends in the TFP and dichotomous sampler data are in agreement. The TFP is not as selective as the dichotomous in two respects: 1) the cut point between fine and coarse particles is not as sharply defined, 2) the upper cut point of the coarse fraction is not defined; in fact, since the large particle TFP is

exposed directly to the atmosphere, any particle which is entrained in the air stream will reach the filter. The sample volume over a 24-hour period is about 1.5 m^3 and 20 m^3 for the TFP and the dichotomous sampler, respectively. Consequently, the precision of the dichotomous sampler data is expected to be better.

The fine particle results for the TFP show fair agreement with the dichotomous sampler results for sulfur and lead. The peculiarly high values for aluminum in the former may be due to problems with the least-squares spectral analysis for the very low energy aluminum x-ray.

The coarse particle results show that, in general, the TFP values are higher than those from the dichotomous sampler. The following results are consistent with the properties of the sampling systems: the TFP sulfur results are high because the fine and coarse particle fractions are not sharply separated; therefore, some of the fine particle sulfur remains on the coarse particle filter. As there is no large particle cut off for the TFP, the elements found in large particles will be more abundant in the TFP coarse fraction than in the dichotomous coarse fraction. This effect would explain the large chlorine values in the TFP data if one assumes that the chlorine is associated with very large particles, e.g., sea salt.

BIOGENIC RELEASE OF SULFUR IN GASEOUS FORM

One of the interesting discoveries of the study was the entirely different nature of the sulfur gases emitted from the different sites. For example, at Site A-1, by far the highest concentration of gaseous sulfur was volatilized as $(CH_3)_2S$, while at Site A-2, H_2S was by far the most prevalent. Figures 23 and 24 substantiate these observations by showing chromatograms of samples taken at the two sites. The chromatograms from Site C were similar to those from Site A-2, while the chromatograms from Site B showed both H_2S and $(CH_3)_2S$.

The concentrations of sulfur gases from the chamber varied considerably depending on time and location. Figures 25 and 26 show two 1½-day periods. During each period the chamber remained at one fixed location, Site A-1, operating continuously. Soil temperature, ambient temperature, and flow rate were recorded after each sampling for the data represented in Figure 26. Ambient temperature and flow rate were recorded less frequently for the data represented in Figure 25. The data shows a significant diurnal variation, apparently due to temperature changes, as well as some fine structure which appears to be correlated with tidal variations. High and low tides are shown by H and L, respectively. The correlation between chamber concentration and temperature is shown more explicitly in Figures 27 and 28. As indicated in these figures, the release of $(CH_3)_2S$ during periods of increasing and decreasing concentration is an exponential function of the temperature from August 31 to September 1. On these days the effect of the tide sustained

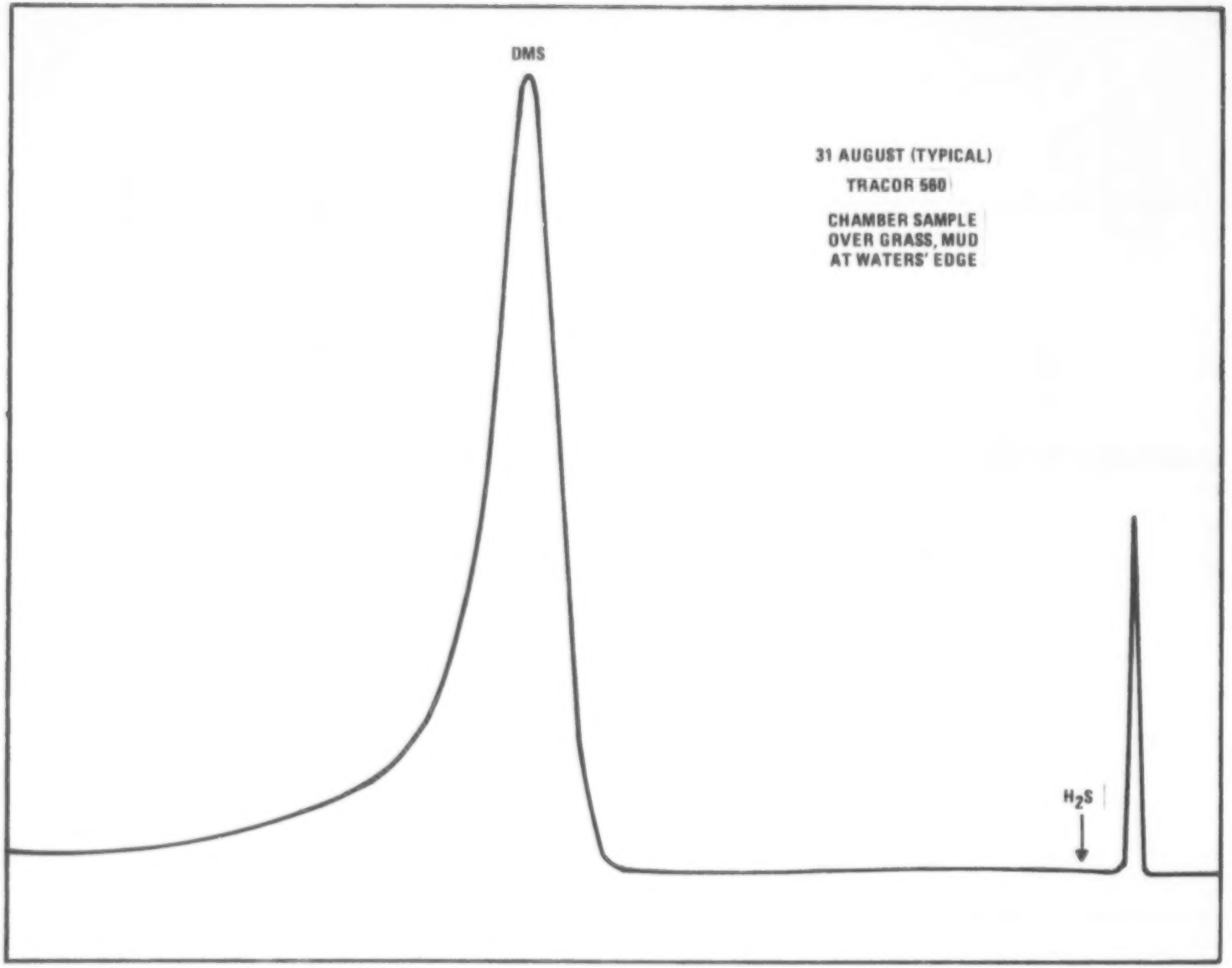

Figure 23. Gas chromatographic analysis of an air sample taken from the environmental chamber at Site A-1. Dimethyl sulfide is dominant.

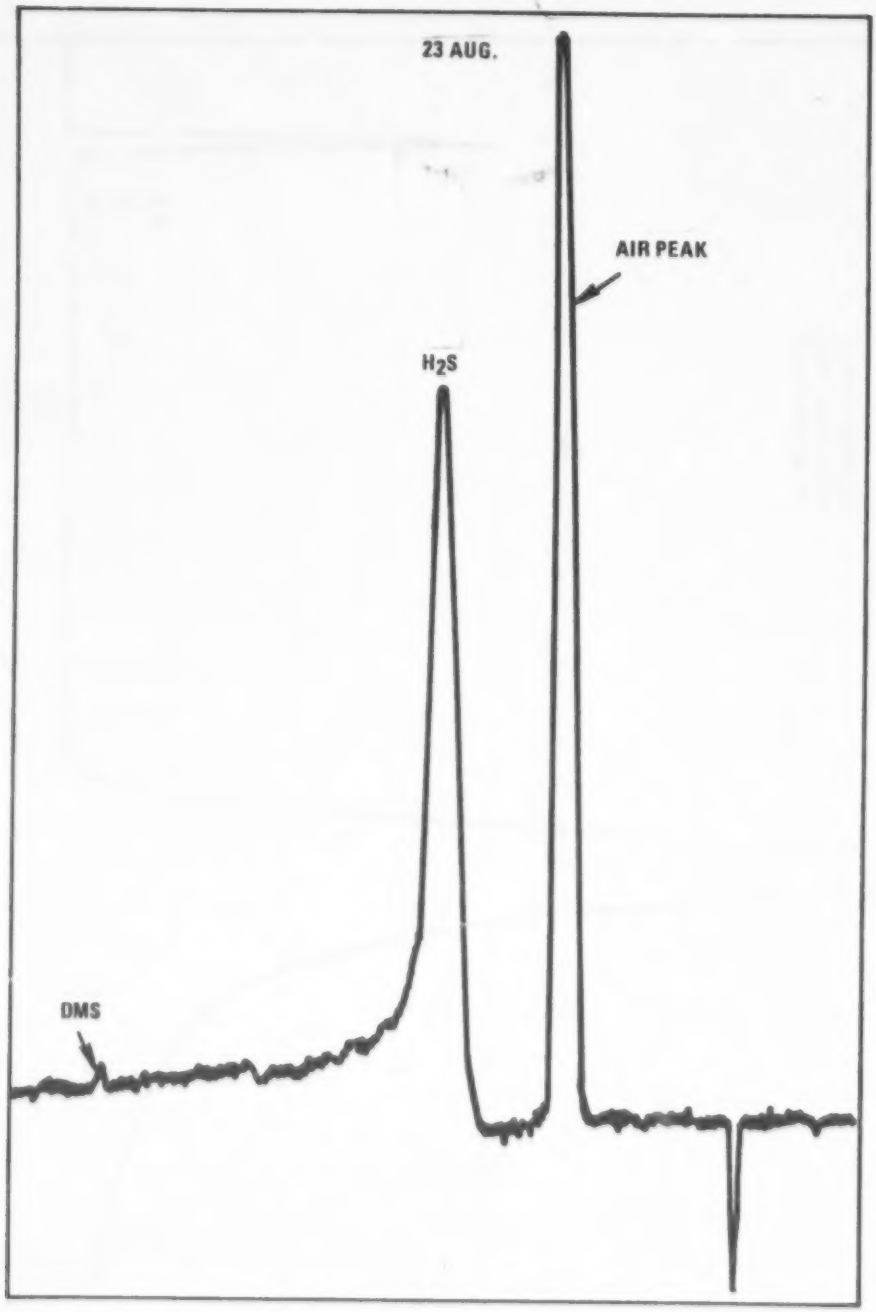

Figure 24. Gas chromatographic analysis at Site A-2 Hydrogen sulfide is dominant.

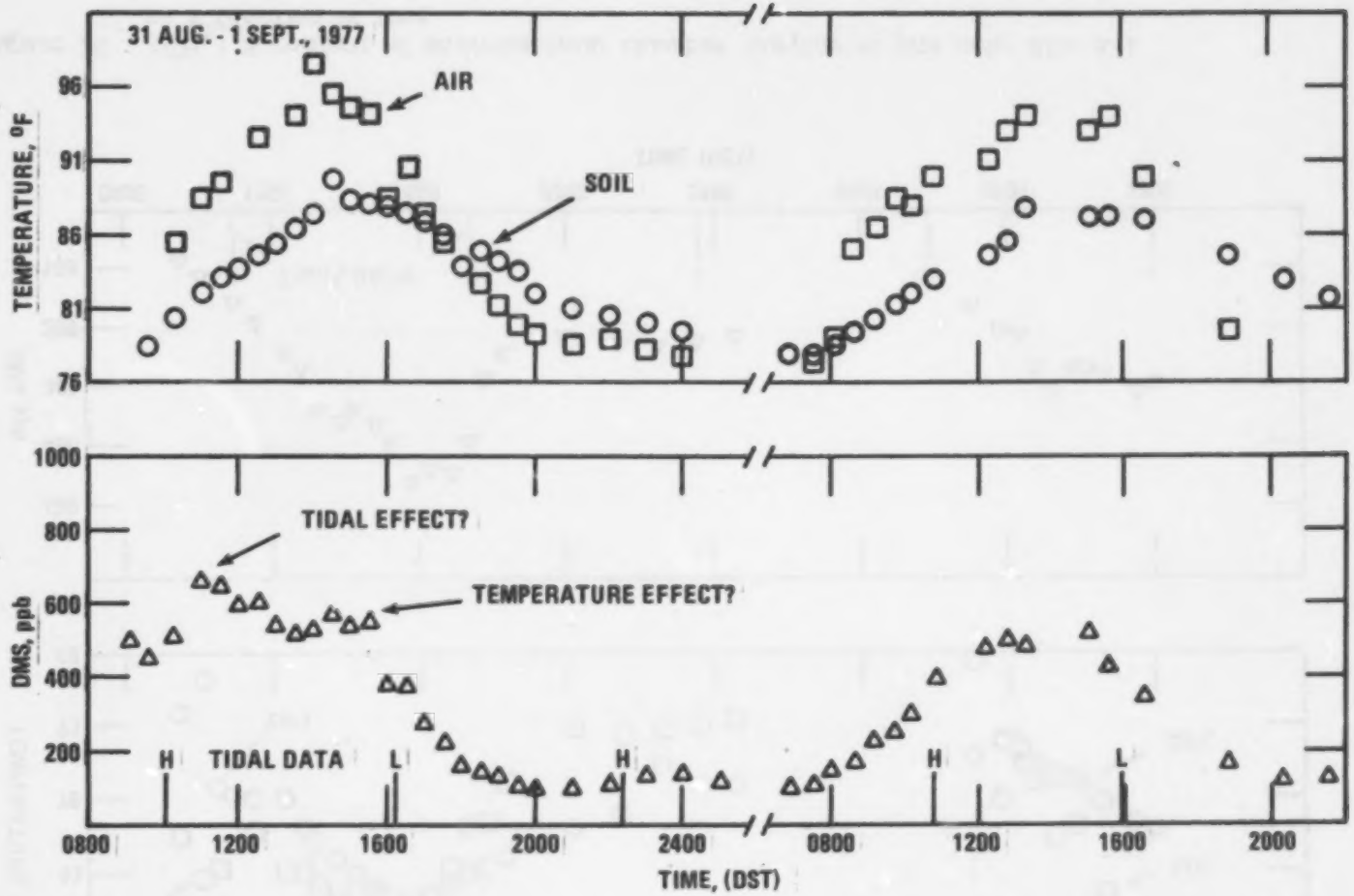

Figure 25. $(CH_3)_2S$ content of environmental chamber samples at site A-1 (edgewater) as a function of time.

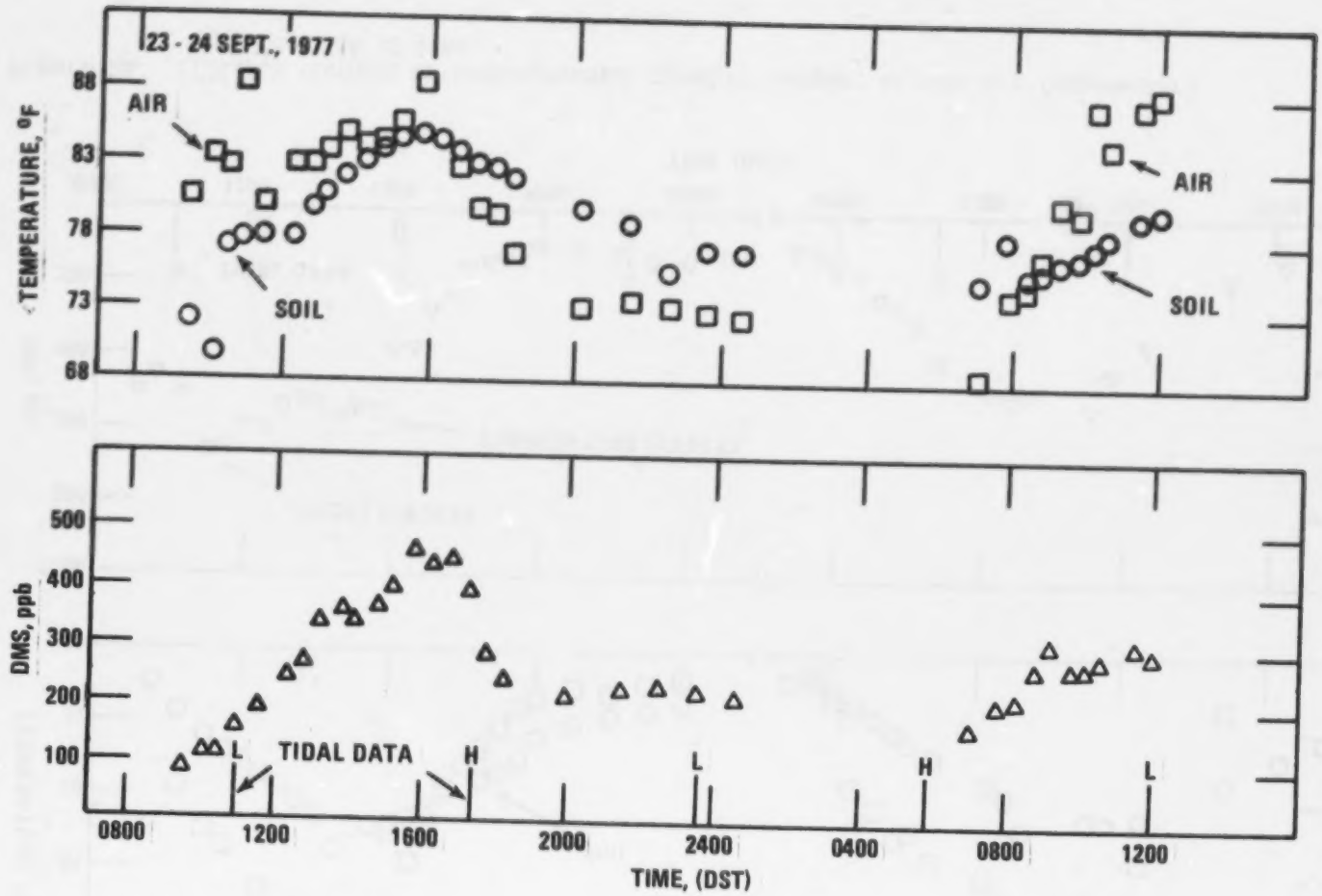

Figure 26. $(CH_3)_2S$ content of environmental chamber samples at site near Site A-1 as a function of time.

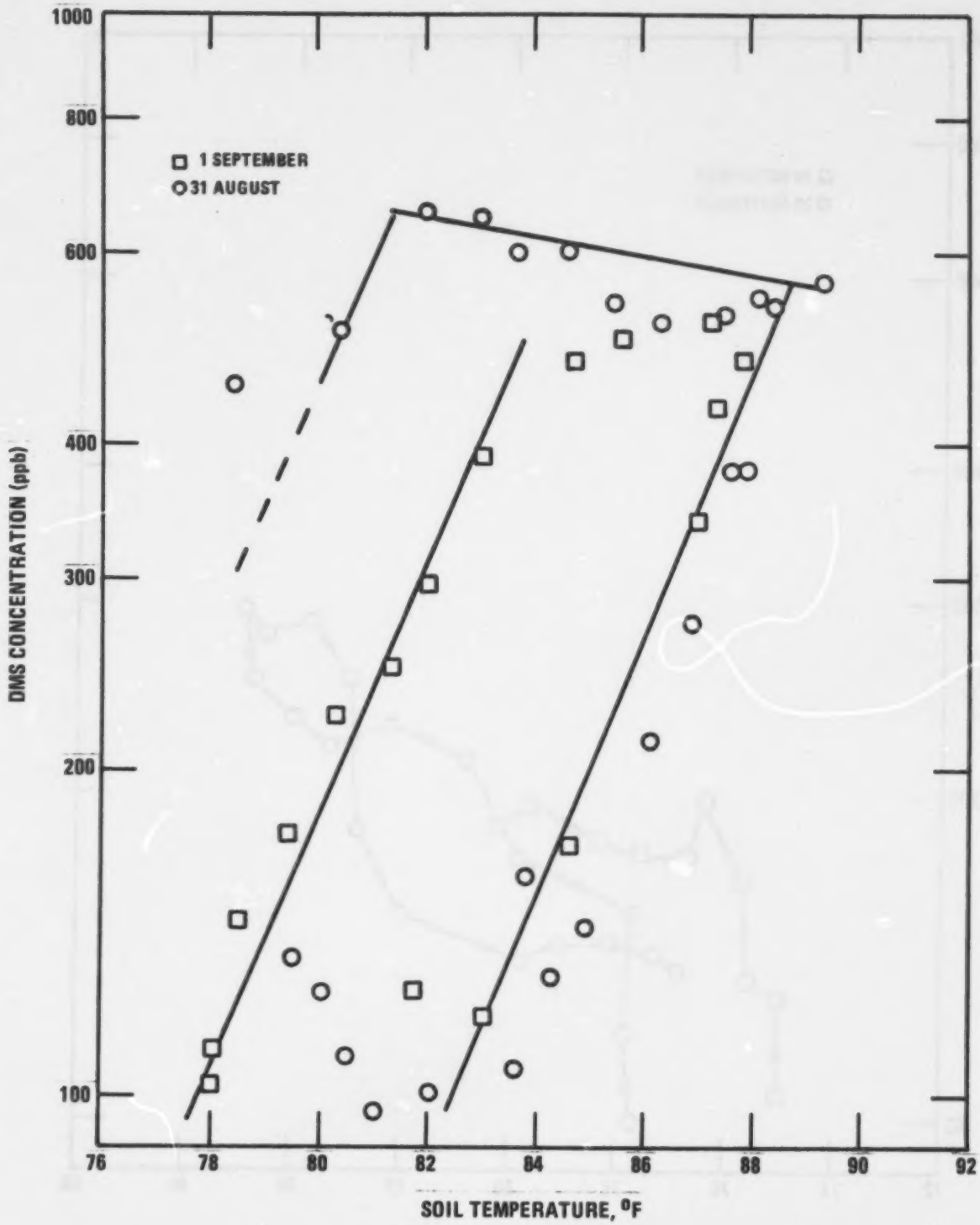

Figure 27. $(CH_3)_2S$ content of environemntal chamber samples (same as Figure 25) as a function of temperature.

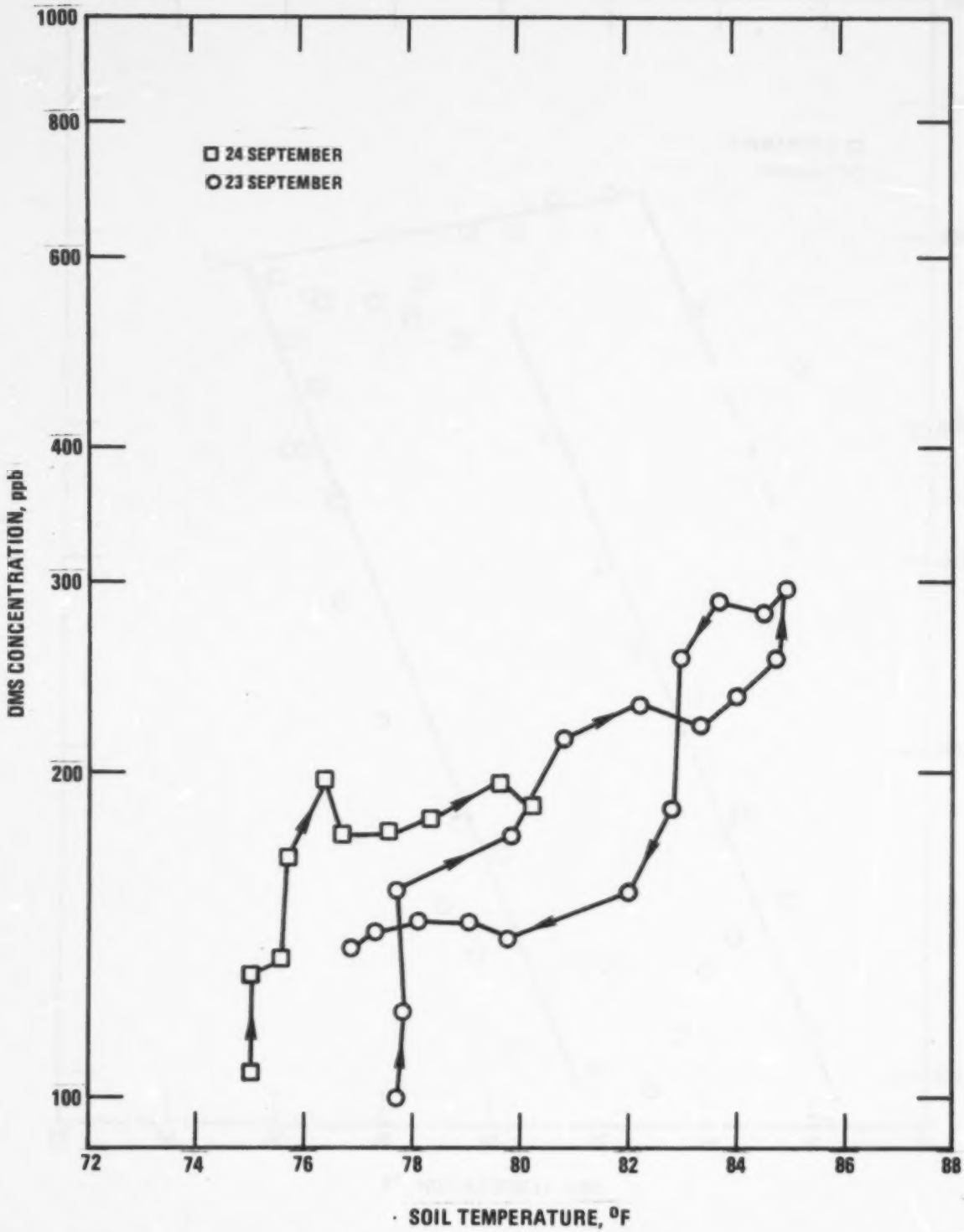

Figure 28. $(CH_3)_2S$ content of environmental chamber samples (Same as Figure 26) as a function of temperature.

the high emission rate of $(CH_3)_2S$ in the interval between high tide and the soil temperature maximum. Since the tidal day is 50 minutes longer than the calendar day, the interval between high tide and the occurrence of maximum soil temperature was shorter on September 1 than on August 31 and the daily release of $(CH_3)_2S$ was less. The release reached a steady value due possibly to a limiting environmental condition such as the availability of reactants or the accumulation of waste products, i.e., pollution in the bacterial environment. If bacteria are producing the $(CH_3)_2S$, the accumulation of waste could accelerate bacterial losses until growth and destruction balance and a steady state population is achieved.

The two days September 23 and 24 were accompanied by tidal variations caused by local winds and variations in cloud cover. There was again a rough exponential correspondence between $(CH_3)_2S$ and soil temperature and the maximum values achieved during the day were less than those which occured on August 31 and September 1.

Other chamber measurements taken on the marsh (Site B) are shown in Figure 29. Chromatograms of chamber samples indicate comparable amounts of H_2S and $(CH_3)_2S$ at total sulfur concentrations about one order of magnitude lower than those found at edgewater (Site A). Site B is on ground seldom covered with water during high tide and seems to be representative of the roughly 4 square miles of marsh between Cedar Island and the mainland.

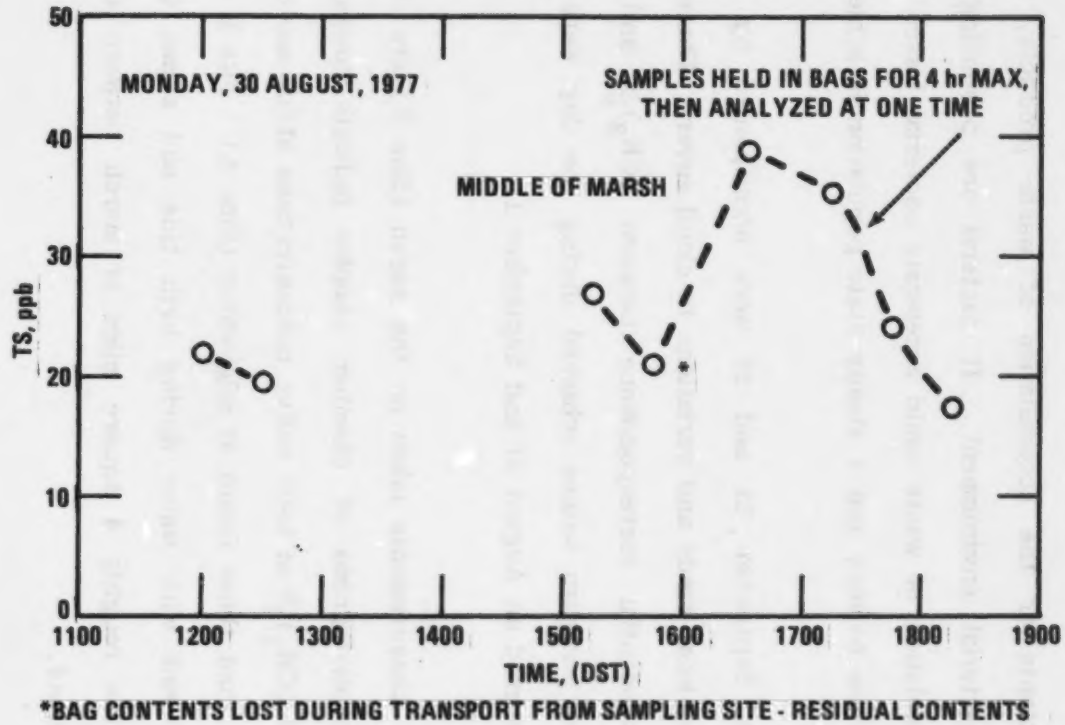

Figure 29. Total sulfur content of environmental chamber samples as a function of time at site B

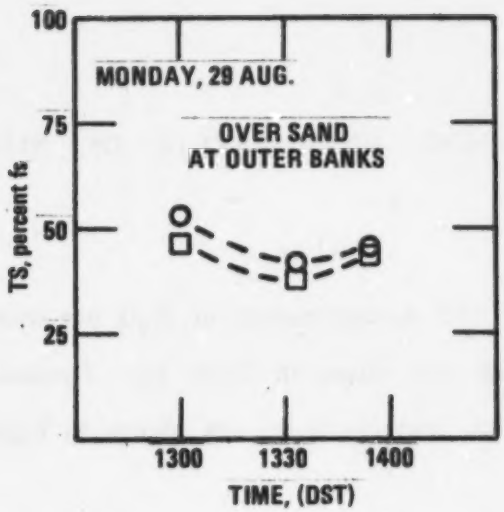

Figure 30. Total sulfur content of environmental chamber samples as a function of time at Site C.

A limited number of measurements were taken over sand on the Outer Banks. Measurements on the afternoon of August 29 are given in Figure 30. Other measurements indicated that the occurrence of a high tide during sampling coincided with high H_2S values. On one occasion a level of 1 ppm was obtained just as the tide rose to carry water into the chamber.

ATMOSPHERIC BACKGROUND MEASUREMENTS OF NITROUS OXIDE, FREON 11 AND FREON 12

The results of the CIFS measurements of N_2O are shown in Table 11 while those for the Freons are shown in Table 12. Typical chromatograms for Freon 11 and Freon 12, and for N_2O, are shown in Figures 31 and 32.

Save for the values found for N_2O in container No. 2, the remaining values are in agreement with those currently reported from other laboratories (16). These results also agree with analytical data obtained in our laboratory on a sample of rural air collected by the National Bureau of Standards. The significance of the anomalous concentrations reported for container No. 2 is not understood as of this writing.

The lone set of values for Freon 11 and Freon 12 may be compared with data gathered by Hanst, et al. (17), on two days at Atlantic Beach, North Carolina.

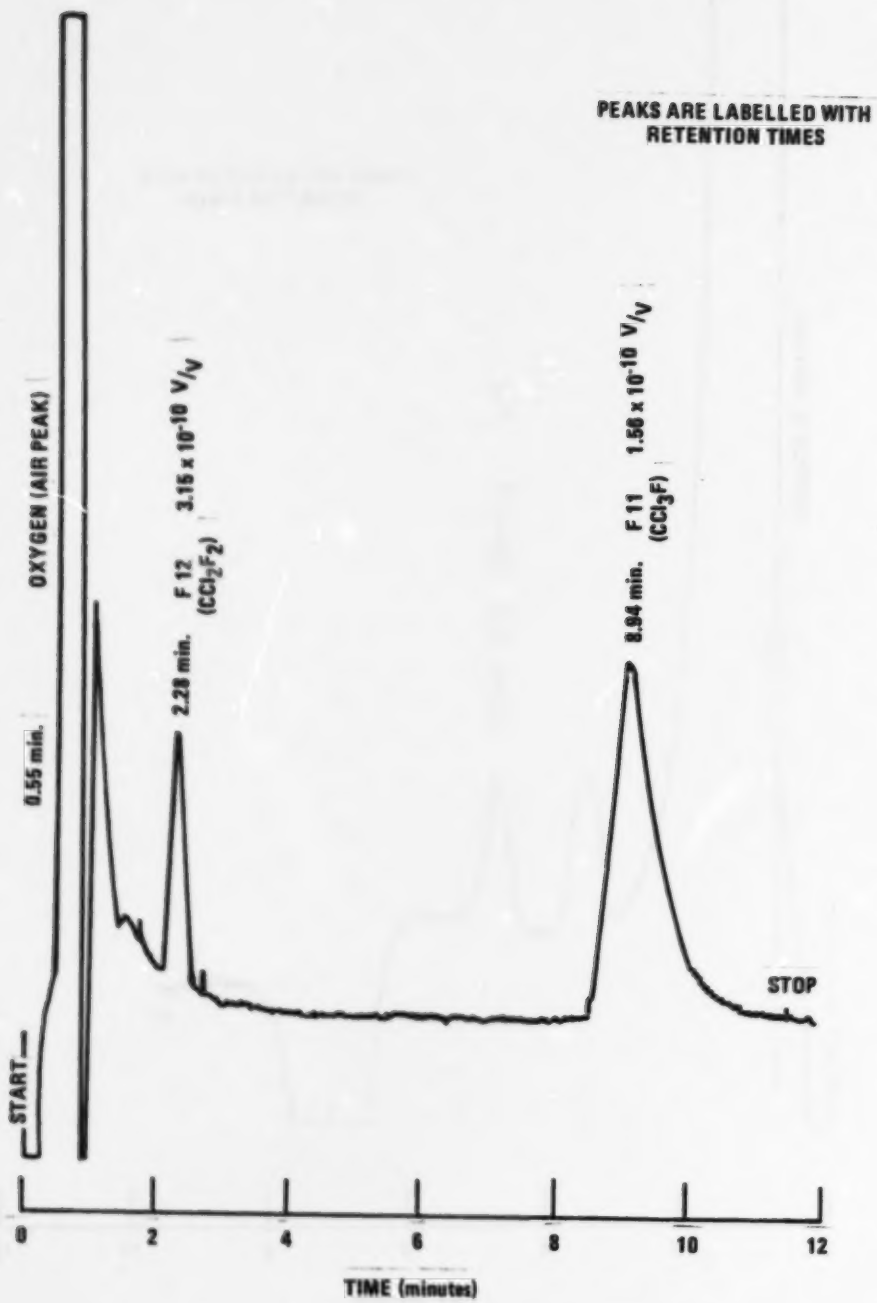

Figure 31. Typical gas chromatographic analysis of Freon 11 and Freon 12.

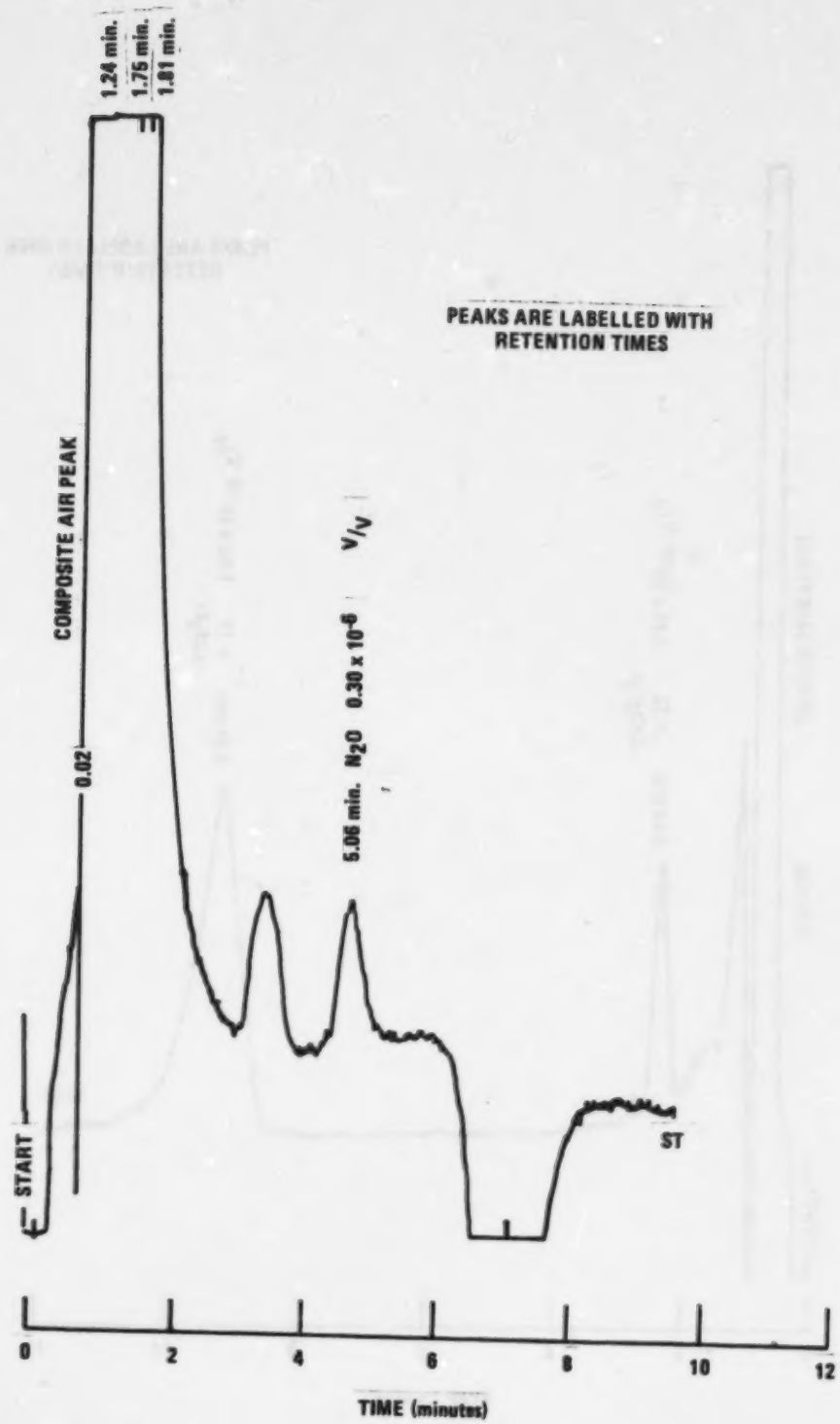

Figure 32. Typical gas chromatographic analysis of N_2O.

TABLE 11. NITROUS OXIDE RESULTS USING GAS CHROMATOGRAPHIC DETECTION

Container	Area (x)	Conc. N_2O (v/v) $(y)^2$
Steel No. 1	869	0.32 x 10-6
	921	0.34 x 10^{-6}
Steel No. 2	1698	0.63 x 10-6
	1776	0.69 x 10^{-6}
Steel No. 3	809	0.30 x 10^{-6}
	792	0.29 x 10^{-6}
Steel No. 4	Insufficient[a]	
Stainless Steel	781	0.29 x 10-6
	845	0.31 x 10^{-6}

Calibration Curve: $y = 3.693\ (10^{-10})\ x = 4.617\ (10^{-9})$

[a]One sample had been removed earlier for Freon analysis. The amount remaining was insufficient for any second run.

TABLE 12. FREONS

Container	Freon 11 (v/v)	Freon 12 (v/v)
Steel No. 4	1.7 x 10^{-10}	2.8 x 10^{-10}

TABLE 13.

Date	Freon 11	Freon 12
5-3-75	1.4 x 10^{-10}	2.9 x 10^{-10}
5-6-75	1.4 x 10^{-10}	1.7 x 10^{-10}

On May 6, 1975 the sample was taken after a storm in clear, breezy weather.

ATMOSPHERIC MEASUREMENTS OF OZONE AND NITROGEN OXIDES

Typical diurnal variations of O_3 and NO_2 dioxide are shown in Figure 33. Similar results were obtained during several days of monitoring. Throughout the tests O_3 concentrations were less than 50 ppb and remarkably constant except for a decrease at night. Due to the low H_2S values and the attendant necessity of sampling over an extended period to accumulate a measurable sample, the influence of O_3 on H_2S or $(CH_3)_2S$ could not be determined.

Nitric oxide and NO_2 concentrations were less than 2 ppb except during the night; thereby confirming the isolation of the site. The increase in NO at night has no apparent cause although the roughly simultaneous decrease in O_3 concentrations indicated that a true NO increase is likely instead of some sampling artifact.

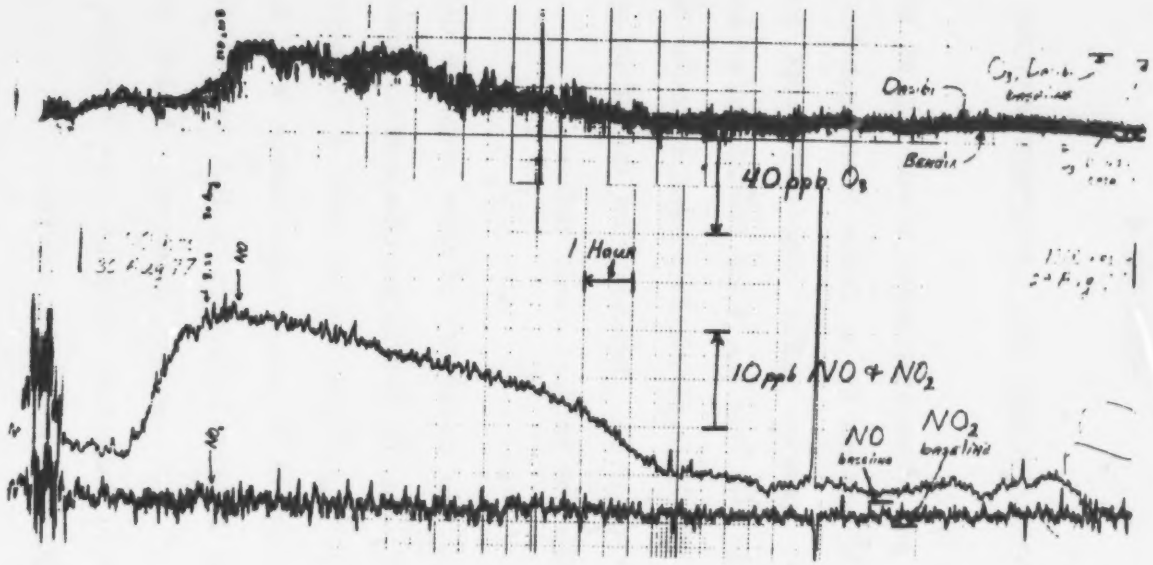

Figure 33. A one day data recording of ambient NO and O_3 concentrations.

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

1. Real time and gas chromatographic monitoring of sulfur gases -- Direct analysis of ambient air at Cedar Island substantiated that the concentrations of gaseous sulfur compounds were consistently less than 5 ppb. The fact that the Meloy SA-285 Sulfur Analyzer and the Tracor 560 Gas Chromatographic-FPD have detection limits of 0.5 ppb and 2-7 ppb, respectively, depending on the sulfur species, makes a precise measurement at ambient levels difficult.

   Recommendations: The possibility of more sensitive detection of H_2S, $(CH_3)_2S$, CH_3SH, etc. by monitoring chemiluminescence with O_3 needs additional study. In-house results with a commercial O_3 monitor adapted for study of O_3 chemiluminescence with H_2S and CH_3SH showed that the relative responses of H_2S and CH_3SH are 1:22 and that 10 ppb of H_2S can be detected. A low pressure system optimized for light collection could be more sensitive than an FPD, especially for gas chromatographic analysis.

2. Preconcentration techniques using gold bead traps -- Development of a trapping technique for sulfur compounds using gold coated glass beads is occurring at the University of South Florida under NSF-RANN sponsorship. The efficiency of collection and release as well as the integrity of sulfur compounds during transfer between analysis system components have been characterized to form a basis for the technique as documented by Ammons and Braman (7). Intercomparison of two calibration standards, i.e., permeation tubes and known solutions of thioacetemide in aqueous solution, gave consistent results and established a sensitivity limit of 0.1-0.2 ng of sulfur with an almost linear response using FPD detection. The calibration precision was $\pm$ 4.9% using 80% confidence limits over a range of 1-50 ng sulfur.

Three features of the technique have been identified as requiring improvement: 1) speciation of heavier molecular weight sulfur compounds (see Figure 16 showing the unresolved group of compounds referred to as RS); 2) blanking of the gold-coated bead trap to establish a "zero" level or blank response; and, 3) use of manpower intensive efforts to sample and analyze.

Recommendation: Continuation of the NSF-RANN grant to South Florida should be encouraged to evolve solutions to the three factors of concern. Automatic samplers should be designed for future studies and an EPA contract or grant effort should be initiated for automation of the analysis phase of the technique.

The glass bead technique has been successfully employed in its initial application. Vertical profiles show increases in sulfur compound concentration with height and a sulfur compound mix that changes with height and the direction of prevalent winds.

Hydrogen sulfide is increasingly responsible for sulfur content as height is increased to 10 meters while $(CH_3)_2S$, $(CH_3)H_2S_2$ and higher molecular weight sulfur-containing compounds are detected near the ground (see Figures 17-21). An unexplained perturbation in the general trend of increasing concentration with height occurs at approximately 1 meter height where an increase in sulfur is seen. Wind masses from the marsh bring more $(CH_3)_2S$, and $(CH_3)_2S_2$ while samples taken in the local pine forest show heavier sulfur compounds.

3. Biogenic emissions -- Chamber studies coupled with GC-FPD measurements were used to identify the mix of sulfur compounds originating from the marsh and to identify pertinent parameters effecting the release of these compounds. The majority of measurements were made over uncut marsh grass near edgewater locations where water was carried into the chamber during measurement.

Differences in the mix of biogenic emissions from sand and marsh were observed using an environmental chamber. Dimethyl sulfide is prevalent over the edgewater marsh areas, H_2S over sand

areas; both compounds occur in the main marsh area. Edgewater emissions are estimated to be an order of magnitude higher than emissions in the marsh, i.e., roughly 10 $g/m^2/yr$ as compared to 1 $g/m^2/yr$. Diurnal variations in chamber concentrations were observed to correlate with soil temperature. Tidal effects appear to be supported by existing data but need additional confirmation. Both H_2S and $(CH_3)_2S$ were detected in the ambient air, using the previously described gold gead technique, when sampling of air masses from the marsh areas was performed. However the measurement of $(CH_3)_2S_2$ and higher molecular weight, S-containing compounds in the ambient air could not be satisfactorily related to evolution from the Cedar Island marshes.

Because stirring of the volume enclosed by the environmental chamber was precluded by the presence of marsh grass, questions related to channeling of the air from chamber inlet to outlet arose. These questions were answered by examining data taken during a period of measurement when chamber concentrations were constant so that the outlet concentration "f" could be measured as function of flow rate "F" to test the model presented on p. 41 of the text. The results are shown in Figures 34 and 35 and suggest that the model agreed with experiment to within ± 20% even though stirring of the chamber volume was not performed. Comparison with a stirred environmental chamber was performed at the beginning of the chamber studies (see Figure 36). Reasonable agreement was obtained after a tight seal has been made around the bottom edge of the chamber.

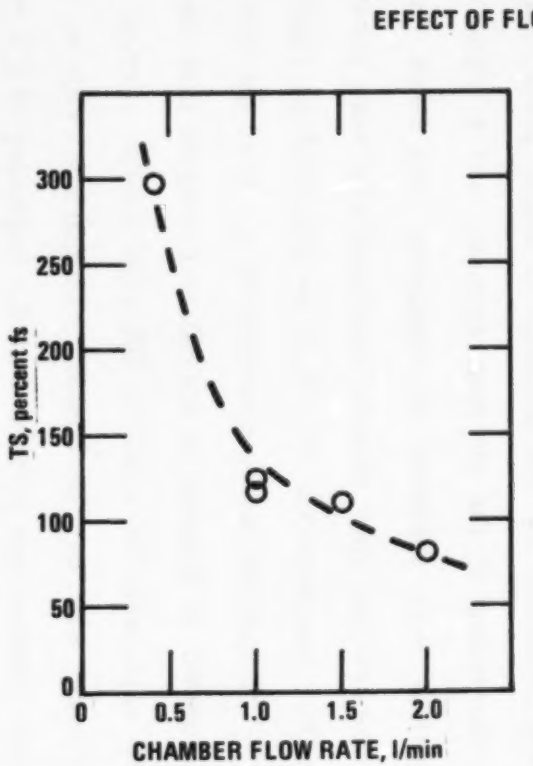

Figure 34. Total sulfur content of environmental chamber samples as a function of flow rate through the chamber

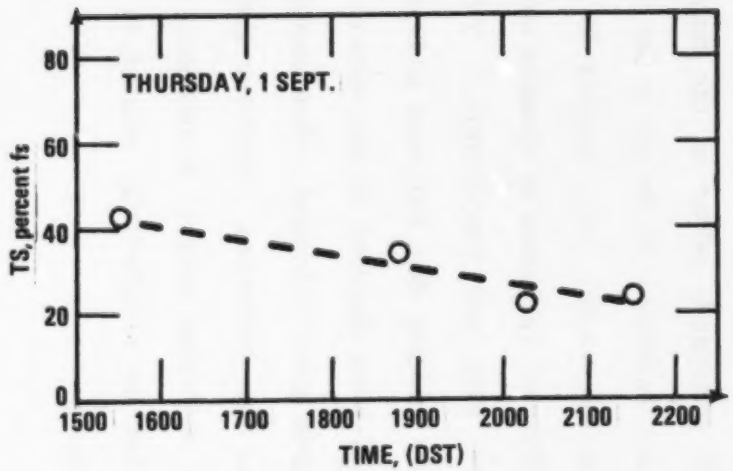

Figure 35. Chamber concnetrations prior to study shown in Figure 34.

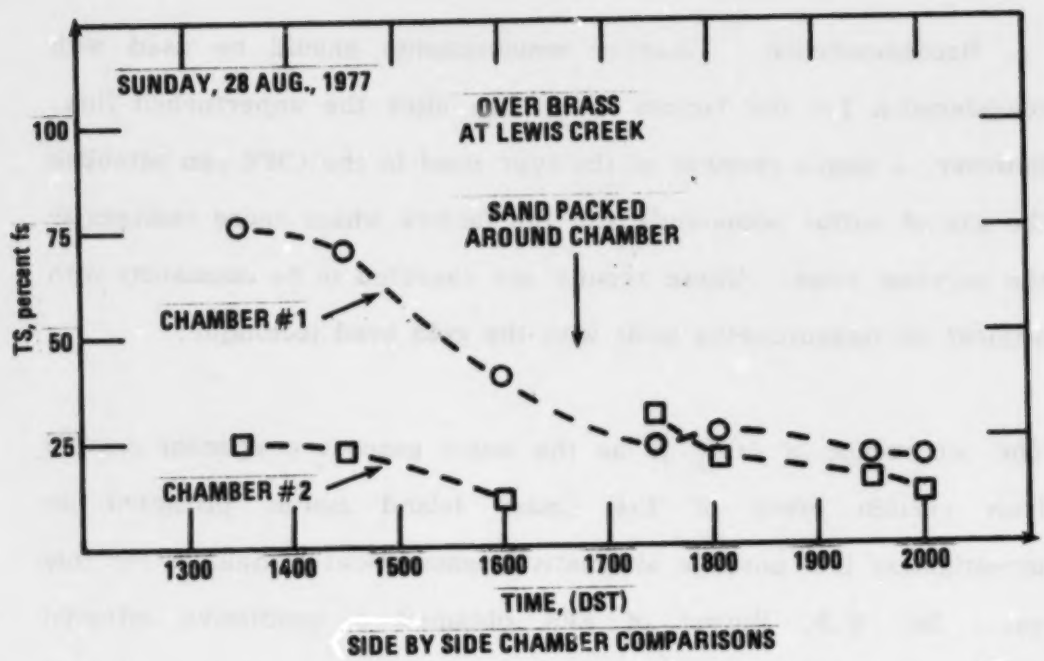

Figure 36. Comparison of results from stirred and unstirred environmental chambers.

The effect of an environmental chamber on the unperturbed flux of sulfur compounds has recently been tested in some detail by Hill, et al. (14).

Recommendation: Chamber measurements should be used with consideration for the factors which can alter the unperturbed flux. However, a simple chamber of the type used in the CIFS can establish the mix of sulfur compounds and the factors which cause changes in the emission rates. These results are expected to be consistent with ambient air measuremetns made with the gold bead technique.

4. The occurrence of $(CH_3)_2S$ as the major gaseous component emitted from certain areas of the Cedar Island marsh prompted an investigation into possible alternative measurement techniques for this gas. Dr. W.F. Herget of EPA obtained a qualitative infrared absorption spectrum of this gas (see Figure 37). An indication of significant absorption in the spectral region around 10.5 microns led to a measurement of the absorption coefficient at CO_2 laser line positions in this region. The results, obtained by Mr. Richard Richmond, of Northrop Services are listed below:

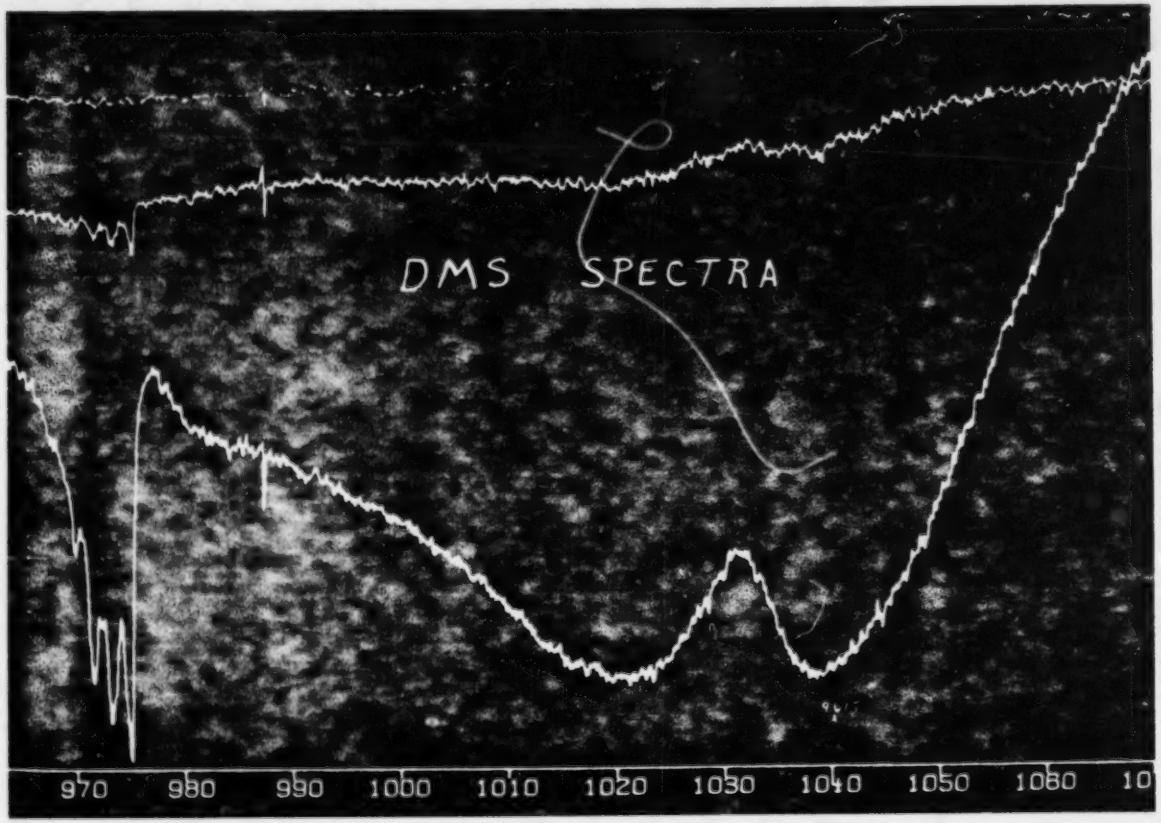

Figure 37. $(CH_3)_2S$ Infrared Spectrum (60-1070 cm^{-1}); top trace indicated zero absorption.

CO_2 laser line	R(14)	10.286 μm	6.2 $atm^{-1}cm^{-1}$
	R(16)	10.272 μm	13.6 $atm^{-1}cm^{-1}$
	R(18)	10.258 μm	11.6 $atm^{-1}cm^{-1}$.

Although these measurements are tentative, they suggest the possibility of measuring $(CH_3)_2S$ by an optical technique, i.e., by either an optoacoustic technique or a long path absorption technique. The measurement of gas emissions as an integrated average over a horizontal distance of several hundred meters at several heights would allow emission rate measurements to be inferred. This technique would eliminate the uncertainties associated with localized measurements. Such measurements appear feasible for gases such as CO_2, CO, N_2O, NO, NH_3, and $(CH_3)_2S$, depending on the actual levels of concentration above the emitting area.

5. Elemental analysis of x-ray fluorescence of fine and coarse particle fractions collected by the dichotomous sampler and the tandem filter pack showed rough agreement between these two collection devices. The tandem filter system is not capable of reproducing the collection properties of the dichotomous sampler, but can provide approximate data for suspended particulates. The dichotomous sampler used in these experiments may have had a plugged coarse particle inlet. This sampler was an early two-stage model and more recent one-stage designs are expected to avoid this possible difficulty.

5. Determination of atmospheric SO_2 by the FPD (short collection times) and the tandem filters (long collection times) were consistent. Detailed comparison is not possible because ambient SO_2 levels were often at or below the FPD's minimum detection level.

6. Determinations of atmospheric H_2S by the glass bead technique (short collection times) and the tandem filters (long collection times) were consistent. Detailed comparison is not possible because of the difference in collection times and the very sensitive dependence of reduced sulfur gas concentration on sampling location, as shown by the height profiles in Figures 17-21.

APPENDIX A

NATURAL SULFUR IN THE ATMOSPHERE

What do the Sulfur Budgets Tell Us?

by

Robert W. Shaw

SECTION A-1

INTRODUCTION

A controversy has existed for some years concerning the relative contributions from man-associated and natural processes to the level of sulfur compounds in the atmosphere. Not surprisingly, the bulk contribution from man-associated activities are much better known than those from natural processes. In an effort to understand the flux of sulfur compounds through the atmosphere, some authors have devised budgets of the "sulfur cycle." These budgets have the following common characteristics: 1) they divide the earth into compartments -- generally lands, oceans and atmosphere; 2) various theoretically and experimentally derived values for concentration of sulfur compounds (the input values) are used to estimate flow between compartments; and 3) a "balance" between flows in and flows out is assumed for one particular compartment, and this balance constraint allows one to infer any sulfur flux not accounted for by the estimated input values. This inferred flux (the output value) is the contribution from natural processes for the sulfur cycle models discussed here.

The various budgets differ in their choice of input values and their balance constraints. It is my purpose here, to summarize the various budget input values and constraints. It will become clear that the

natural sulfur contributions inferred by different authors are very sensitive to the characteristics of the models used. These comments are not critical of the global sulfur cycle models; the uncertainties of budget-derived sulfur fluxes are well understood by their authors. The papers described here may also serve as evaluations and guides to the literature of atmospheric chemistry and its characterization, and the sulfur budgets are only part of these interesting publications. This paper is simply intended to help judge the significance of the magnitudes of natural sulfur fluxes derived from global sulfur budgets. In the following section, budget inputs and constraints will be presented very briefly with no discussion of their validity or plausibility; for these the reader is referred to the original articles. In Section A-3 the implications of using a number of model calculations are discussed. The models are approximate, as are the budgets themselves; they serve as order-of-magnitude indications of the consequences of the natural sulfur evolution rate values. In Section A-4 the measurement of natural sulfur is discussed. The summary and conclusions are in Section A-5.

SECTION A-2

DESCRIPTION OF THE MODELS

Junge (19) has developed a sulfur budget based on a balance in the atmosphere; his values are given in Table A-1. According to Junge, the best known sulfur source is industrial (40 MT/yr, 1 MT = 10^6 tons), and the best known sink is precipitation (70 MT/yr). Junge assumes that natural evolution of sulfur from the land (70 MT/yr) is balanced by "direct uptake." Since the amount of sulfur in precipitation over land exceeds the industrial output by 30 MT/yr, this amount must be supplied by the ocean. The "direct uptake" by the ocean is 70 MT/yr, the precipitation contribution is 60 MT/yr. Therefore, the ocean must supply 160 MT/yr of natural sulfur to balance the atmosphere.

Notice that in this budget, the natural evolution and absorption over land are equal and form a closed system with no effect on the other compartments of the model. A consequence of the budget is the accumulation of sulfur in the ocean as a result of river run-off. This budget proposes total sulfur evolution from natural sources of 230 MT/yr; of this, 140 MT/yr is absorbed by direct uptake. Nothing is known about

the lifetime of the uptake process; within the limit of short lifetimes for evolution-absorption there would be no contribution to the atmospheric sulfur burden. A possible measure of the natural contribution to sulfur in the atmosphere over land is given by the net sea to land flux of 30 MT/yr.

Kellog, et al. (20), developed a global sulfur budget which is similar to that of Junge. Sulfur sources to and sinks from the atmosphere are brought into balance by including the necessary flux from natural sources. Values from their budget are given in Table A-1. Their inferred value for naturally evolved sulfur is 89 MT/yr; it is much lower than Junge's value because: 1) the dry deposition for sulfur over land is much lower; 2) the dry deposition over ocean is zero; and 3) part of the wet deposition over the ocean is supplied by sea spray. A consequence of the budget by Kellog, et al. is that the net sulfur flux through the atmosphere occurs from the land to sea.

An interesting global sulfur budget has been presented by Hallberg (21) who has estimated a pre-industrial sulfur cycle. Again, the sources to and the sinks from the atmosphere are balanced; but, unlike the previous budgets, another balance is included -- a steady state of the pedosphere. Inputs to the pedosphere are weathering, sea spray, and wet and dry deposition; outputs are river run off and natural evolution. The budget values are given in Table A-1.

In Hallberg's budget the natural contribution of evolved sulfur compounds is inferred by satisfying the balance requirements for the pedosphere; it is about one sixth that estimated by Junge and one half that estimated by Kellog, et al. The lower value for natural sulfur is due to the values for wet and dry deposition. These wet and dry deposition rates are themselves inferred from the balance requirement for the atmosphere. A consequence of the budget by Hallberg is that a pre-industrial net sulfur flux from sea to land is reversed by industrial output to become a net flux from land to sea.

Granat (22) has presented a global atmospheric budget in a companion paper to that by Hallberg. Granat's budget emphasizes the sources of sulfur in submicron particles. Granat assumes a balance in the atmosphere and, from an independent review of the literature, develops a budget which agrees well with Hallberg's results (see Table A-1). Both Granat and Hallberg point out that earlier sulfur budgets included sulfur deposition rates which depended on a rather scant and uncertain data base. These sulfur concentration data may have been high because of influences of distant pollution sources. Only recently have workers appreciated the influence of, for example, industrial centers in creating pollution episodes hundreds of kilometers away; hence the early estimates of global deposition rates and the consequent natural evolution rates may have been too high.

SECTION A-3

DISCUSSION

Our interest here is in the information derived from the budgets concerning the relative contributions of sulfur compounds to the atmosphere by man and by nature. As we have seen, the estimated natural contributions range from 40-230 MT/yr. Can one then assume with confidence that the real value lies somewhere between these limits? I believe not. As we have already seen, these values are inferred from a balance condition and depend on values for deposition rates over the entire surface of the earth. The balance condition, i.e., that the inputs to and the outputs from the atmosphere are equal, appears plausible. Very little is known, however, about global deposition rates.

We next examine the implications of the budgets on sulfur burdens in the atmosphere. As the authors of the budgets recognized and discussed at some length, little is known concerning the lifetimes of sulfur compounds in the atmosphere especially from natural sources. The relation between lifetime and sulfur burden becomes visible in a rough way when considering a system with sulfur input rate "I" (MT/yr), total sulfur burden "S" (MT) and output rate constant "λ" (yr^{-1}). Then:

$$\frac{dS}{dt} = I - \lambda S \ ,$$

$$\lambda S = I\ (1 - e^{-\lambda t}) \ ,$$

$$S = \frac{I}{\lambda}\ (1 - e^{-\lambda t}) \ .$$

This expression shows that the sulfur burden will approach a steady state value of I/λ. Since the halflife "$t_{\frac{1}{2}}$" is equal to $\ln 2/\lambda$, the sulfur burden is directly proportional to the atmospheric lifetime.

Table A-2 shows a number of steady state atmospheric sulfur burdens that are due to the natural evolution rates taken from two of the global sulfur budgets described above for a number of assumed atmospheric sulfur half lives (1 day and 10 days); the simple expression derived above was used. The burden has been expressed in ppb (v/v) by taking the mass of the atmosphere to be 5×10^{21} gm (23) and assuming one sulfur atom per molecule. Table 2 gives the results for two assumptions for mixing: 1) the sulfur compounds mix uniformly throughout the entire atmosphere; 2) mixing occurs uniformly throughout the atmosphere below the altitude of 1 km (approximately 11% of the atmosphere lies below 1 km. In this calculation it is assumed that naturally evolved sulfur compounds are spread uniformly through their mixing volume and that all have the same half life. The wide range of values in Table A-22 shows the sensitivity of steady state atmospheric sulfur concentrations to assumed evolution rates and atmospheric lifetimes.

The calculation just outlined is very crude; as mentioned above, it assumes that the sulfur compounds are uniformly mixed throughout their mixing volume in the atmosphere. In fact, since they are injected into the atmosphere from the land or from a sea surface and leave the atmosphere through these surfaces, a gradient will exist, the highest concentration being at the surface. Since we live mostly at or near these surfaces, these higher concentrations are most important; the calculation, however, only roughly indicates a lower limit.

SECTION A-4

MEASUREMENT OF NATURAL SULFUR IN THE ATMOSPHERE

The estimated ratio of the natural evolution of sulfur compounds to man-associated (industrial) evolution in the models described above ranges from 6/1 (19) to 1/2 (22). Although one may argue that more recent data were available to Granat than to Junge, the budgets themselves present no compelling evidence that the natural sulfur evolution rates may not be even larger than those estimated by Junge or alternatively, even smaller than those by Granat. It is clear that resolution of this question would require at least the following: 1) measurement of natural evolution rates of sulfur, and 2) identification of the compounds evolved.

There are two means of estimating natural sulfur evolution rates: 1) by direct measurement, 2) indirectly, by inferrring the natural sulfur "background" levels from measurement of atmospheric samples in areas not affected by mean-associated activities. The best procedure may be a judicious combination of these two methods. The indirect method is complicated by at least two factors: 1) measurements of atmospheric samples may be affected by long range effects of distant industrial or urban pollution sources, 2) evolved sulfur compounds are immediately diluted by the atmosphere in a complex and, presumably, varying manner.

Direct measurement can be carried out by placing an enclosure over the surface to be studied and sampling the sulfur compounds, if any, as they evolve into it. A system of this sort has been described by Aneja (13) and others; workers at the EPA are now evaluating the use of sampling enclosures in the field (this report). The application of gas chromatography to the collected sample provides separation and identification of the evolved sulfur compounds. Any sampling program which uses enclosures will have to examine the effect, if any, of the enclosure itself on the evolution rates.

The obvious difficulty with direct measurement is the need for sufficient local data to characterize adequately a global process. Some investigators believe that most natural sulfur evolution occurs from marshy and estuarine areas. If this is so, and if the sulfur evolution from a given marsh can be correlated with some large scale characteristics of the marsh, e.g. soil composition, the problem reduces to one of determining the sulfur evolution from the various types of marsh and multiplying by the total area of these marshes.

SECTION A-5

SUMMARY AND CONCLUSIONS

The required evolution of sulfur compounds from marsh areas may be estimated according to the various global sulfur budgets by assuming the following: 1) that all marshes emit uniformly; 2) that all other natural sulfur sources are negligible; and 3) by taking the total marsh area as 2.8 x 10^5 km^2 (25). By simply dividing the evolution rates by the emitting area, we find that the sulfur budgets of Junge and Granat demand evolution rates of 750 and 120 $g/m^2/yr$, respectively. The sulfur evolution rate may also be calculated, if all the land surfaces of the earth (1.5 x 10^8 km^2) emit uniformly; these rates are 1.4 $g/m^2/yr$ and 0.22 $g/m^2/yr$ for the Junge and Granat budgets, respectively.

The calculation is a crude one; however it does serve to tabulate the natural sulfur evolution rates from the sulfur budgets so that they may be compared with the experimental measurements. In Table A-33 the results from these calculations are compared with the measurements for sulfur evolution made by Aneja (13) in the Long Island tidal marshes and by McClenny, et al. (this report) in the North Carolina tidal marshes. In these experiments, sampling enclosures were used and the sulfur compounds were identified using gas chromatography. Aneja's

measurements were made in October and November, 1974, during the day with soil sediment temperatures ranging from 6.6-17.6°C. He remarks that his highest value for H_2S, 39 $g/m^2/yr$ is "anomalously high." The averages were calculated neglecting the "anomalously high" value and also neglecting zero measurements. The averages shown for the measurements by McClenny made in August, 1977, also neglect any zero values.

The experimental measurements may now be compared with the expected evolution rates based on the sulfur budgets and assuming that only marsh lands evolve sulfur. According to Table A-3, the evolution rates of sulfur compounds from experimental sites the on Long Island and North Carolina marshes are 100-1000 times lower than expected from the sulfur budgets. Therefore, if marshlands are the most important sources of natural atmospheric sulfur, and, if the sulfur budget values for natural sulfur evolution rates are correct, somewhere there must exist very high sulfur producing marshes.

TABLE A-1. PRINCIPAL ELEMENTS IN THE GLOBAL SULFUR BUDGETS (MT/yr)

	LAND				SEA				Net Sulfur Flux Through Atmosphere	
	Evolution		Deposition		Evolution		Deposition			
	Industrial	Natural	Wet	Dry	Spray	Natural	Wet	Dry	Land → Sea	Sea → Land
Junge	40	<u>70</u>	70	70		160[c]	60	70		30
Kellog, et al.	50	<u>89</u>[a]	86	25	43		72		29	
Hallberg										
pre-industrial:	0	<u>3</u>		23[b]	48[d]	<u>37</u>		21[b]		17
present:	72	<u>3</u>		<u>77</u>[b]	48[d]	<u>37</u>		39[b]	1	
Granat	72	<u>6</u>	55	40	48	<u>30</u>[e]	61	2		14

Underlined values are derived from balance constraints.

a) Natural evolution occurs from land and "coastal areas." b) wet + dry deposition. c) Natural evolution occurs from "sea or coast."
d) Sea spray not included in deposition calculations. e) Natural evolution occurs from land and "coastal areas."

TABLE A-2. STEADY STATE GLOBAL ATMOSPHERIC SULFUR FROM NATURAL SOURCES

Budget	Natural Evolution Rate (MT/yr)	Sulfur Burden (ppb) $t_{1/2}$ = 1 day	10 days
Junge	230	1.4*	14*
		0.15**	1.5**
Granat	36	0.21*	2.1*
		0.023**	0.23**

*Mixing Depth: 1 km (11% of atmosphere)
**Mixing Depth: ∞ (100% of atmosphere)

TABLE A-3. RATES OF NATURAL SULFUR EVOLUTION

A. Model Calculations

Budget	From Marshes Only (2.8×10^{11} m^2)	From All Land Surfaces (1.5×10^{14} m^2)
Junge	750 $g/m^2/yr$	1.4 $g/m^2/yr$
Granat	120 $g/m^2/yr$	0.22 $g/m^2/yr$

B. Experimental Measurements

Location	Sulfur Evolution Rate (g/m^2-yr) H_2S	DMS
Aneja: Long Island coastal marshes (1974)	39 (max)	2.0 (max)
	0.33 (av)	1.4 (av)
McClenny: North Carolina -- coastal marshes (1977)	7.8 (max)	5.5 (max)
	0.5 (av)	0.3 (av)

APPENDIX B

OPERATING CHARACTERISTICS OF THE SULFUR MONITOR USED AT CEDAR ISLAND

by

R.W. Shaw

This section briefly describes the response of the Meloy SA 285 FPD used at Cedar Island to CO_2; Water Vapor, and In-line Scrubbers.

Bench tests run at EPA laboratories have shown that CO_2 will cause the detector response to sulfur to decrease. Over the range 0-150 ppb SO_2, the presence of 350 ppm CO_2 causes a nearly linear decrease in response of 10%. If, however, the instrument is calibrated in the presence of 350 ppm CO_2, the reproducibility and linearity of response are excellent. Similarly, water vapor causes decreased response in the detector. For example, a change from 0-100% relative humidity at 22°C causes a depression of the zero response by an amount equivalent to 3 ppb SO_2.

In order to adjust the instrument response for the effects of CO_2 and water vapor outlined above, calibrations in the field were made using air containing 350 ppm CO_2 and at approximately 80% relative humidity. These conditions roughly reproduced the properties of the ambient air.

During the field experiments, the sample line into the detector contained a Teflon filter to remove sulfate aerosol particles. In addition, an SO_2 gas scrubber (Meloy Labs) could be moved in and out of the sample line. The level of reduced sulfur gases in the ambient sample was determined by the difference: total sulfur gases minus SO_2. Laboratory

experiments at EPA laboratories indicate that, at 50% relative humidity, SO_2 scrubbers remove 100% of SO_2 down to less than 0.2 ppb and pass 75-90% H_2S. Warming the scrubber improves the H_2S pass-through, but does not bring it up to 100%.

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